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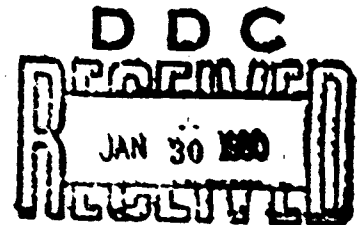Basic Studies Relative to the Syntheses

of

Unsymmetrical Dimethylhydrazine and Monomethylhydrazine

By

Chloramination

University of Florida Part

For Period September 1, 1975 to September 30, 1979

Principal Investigator

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The reactions of chloramine with appropriate nitrogen bases to form unsymmetrical dimethylhydrazine or monomethylhydrazine were examined. Various by-products were identified and mechanisms proposed. Processes for the synthesis of both of these hydrazines were developed. The oxidation of unsymmetrical dimethylhydrazine by gaseous oxygen was studied and the various products identified. The oxidation of monomethylhydrazine was also investigated. The oxidation of unsymmetrical dimethylhydrazine by mercuric oxide was also studied.

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LIST OF ABBREVIATIONS

DMTC	2,2-Dimethyltriazanium Chloride
FDMH	Formaldehyde Dimethylhydrazone
FMH	Formaldehyde Monomethylhydrazone
MMH	Monomethylhydrazine
NDMA	N,N-Dimethylnitrosamine
TMT	1,1,4,1-Tetramethyl-2-tetrazene
UDMH	1,1-Dimethylhydrazine

INTRODUCTION

Unsymmetrical dimethylhydrazine (UDMH), and monomethylhydrazine (MMH), have achieved special importance as high energy rocket[1] and space shuttle fuels. These compounds have large heats of combustion, relatively high densities and high specific impulses. Until recently, UDMH was manufactured by the catalytic hydrogenation of 1,1-dimethylnitrosamine (NDMA). Studies now have shown that NDMA is highly carcinogenic[2]. A search for a new manufacturing process has drawn attention to an earlier publication by Sisler and co-workers[3] which reports the formation of substituted hydrazines by the chloramination of amines.

In order to investigate the utility of the work of Sisler and co-workers for the production of UDMH and MMH, a joint project was undertaken by the Chemical Laboratory at the University of Florida, Gainesville, Florida and the Surface Weapon Center White Oak Laboratory, Silver Spring, Maryland. The project was entitled "Basic Studies Relating to the Syntheses of 1,1-Dimethylhydrazine and Monomethylhydrazine by Chloramination". The project was sponsored by the AFOSR, Directorate of Chemical Research and was funded from September 1, 1975 to September 30, 1979. The research was conducted at both of the laboratories. During the project period, the progress of the research was reported to the AFOSR through the progress reports and project renewal reports on a regular basis[4-7].

The project ended on September 30, 1979 and this is the final report on the University of Florida portion of the project. The report summarizes the significant results achieved at the University of Florida (for more details, please see the progress reports referred to above).

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1. W. E. McQuistion, R. E. Bowen, G. A. Carpenter and G. R. Wilmot, Final Report entitled "Basic Studies Relating to the Synthesis of 1,1-Dimethylhydrazine and Methylhydrazine by Chloramination" AFOSR Directorate of Chemical Sciences. Bolling AFB, Washington, D.C. 20332. March 1979.

2. J. S. Wishnok, J. Chem. Educ.. 54, 440 (1977).

3. Please see the references 2-21 in Appendix I.

4. H. H. Sisler, Progress Report of University of Florida Part of AFOSR Grant No. 76-2915 February 15, 1976.

5. H. H. Sisler, Progress Report to the AFOSR, University of Florida Part, for period April 1, 1976 through November 30, 1977.

6. H. H. Sisler, Proposal to the AFOSR (Including the summary of the results since November 30, 1977). Submitted on July 1978.

7. H. H. Sisler, Progress Report to the AFOSR Period July 1, 1978 to March 1979. University of Florida Part.

SUMMARY OF RESEARCH RESULTS

There follow short abstracts of the principle accomplishments of the
subject grant. In the appendices are complete presentations in the form
of journal articles published, submitted for publication or prepared for
publication and shortly to be submitted.

1. Chloramination of Dimethylamine and 1,1-Dimethylhydrazine.

The chloramination of dimethylamine in a solution of KOH in n-butanol
was carried out in the presence of NH$_3$ at room temperature. The major
products were 1,1-dimethylhydrazine, the dimethylhydrazone of formaldehyde,
and 1,1,4,4-tetramethyl-2-tetrazene. The yield of the hydrazine approximated
30% based on the chloramine used. 1,1-Dimethylhydrazine was reacted with
ammonia-free chloramine in ether solution. The products included CH$_4$,
N$_2$, the dimethylhydrazone of fomaldehyde, and 1,1,4,4-tetramethyl-2-tetra-
zene. The oxidation of 1,1-dimethylhydrazine with HgO, and with Ag$_2$O in
ether, aqueous, and alkaline solutions was carried out. Mechanisms for
the formation of the various oxidation products are proposed.

2. Chloramination of Trimethylhydrazine.

The reaction of chloramine with trimethylhydrazine, (CH$_3$)$_2$NNH(CH$_3$),
has been investigated. The principal product formed when this reaction is
carried out in ether is the dimethylhydrazone of formaldehyde, (CH$_3$)$_2$NN = CH$_2$
The absence of 1,2,2-trimethyltriazanium chloride, the expected product,
is explained in terms of the weaker nucleophilicity of trimethylhydrazine

compared to that of 1,1-dimethylhydrazine, which reacts with chloramine to form 2,2-dimethyltriazanium chloride, $[(CH_3)_2N^+(NH_2)_2]Cl^-$. The principal product of the chloramination of trimethylhydrazine, when the reaction is carried out in acetonitrile, is 2,2-dimethyltriazanium chloride. Mechanisms are proposed for the chloraminations in both solvents. Chloraminations of dimethylhydrazone of formaldehyde and of tetramethyl-2-tetrazene, $(CH_3)_2NN = NN(CH_3)_2$, carried out for purposes of comparison, also resulted in formation of some 2,2-dimethyltriazanium chloride. Attempts to synthesize 1,1,2-trialkyltriazanium chlorides by reaction of 2,2-dimethyltriazanium chloride with alkyl halides were unsuccessful, resulting either in no reaction or in the formation of 2,2-dimethyltriazanium iodide. A mechanisms for the formation of 2,2-dimethyltriazanium chloride by the chloramination of trimethylhydrazine is proposed.

3. Pyrolysis and Hydrolysis of 2,2-Dimethyltriazanium Chloride.

The purification, hydrolysis, and pyrolysis of 2,2-dimethyltriazanium chloride are described. The gas chromatography data indicate that the pyrolysis products in a helium atmosphere are NH_4Cl, N_2 $(CH_3)_2NN=CH_2$, and small amounts of $(CH_3)_2NNH_2$ and $(CH_3)_2NN=NN(CH_3)_2$. Under vacuum, with or without solid NaOH, the products are NH_4Cl, N_2, $(CH_3)_2NN=CH_2$, and trace amounts of $(CH_3)_2NN=NN(CH_3)_2$ but no $(CH_3)_2NNH_2$. The ultraviolet spectroscopy data for the hydrolysate of $(CH_3)_2N(NH_2)_2Cl$ in 0.5-2.0 N KOH solution indicate that $(CH_3)_2NN=CH_2$ is the major product. The value of λ_{max} for $(CH_3)_2NN=CH_2$ is pH dependent and shifts toward shorter wavelengths with increased pH. The rate of formation of $(CH_3)_2NN=CH_2$ follows approximately

first-order kinetics with respect to $(CH_3)_2N(NH_2)_2Cl$. The mechanisms for
the formation of various pyrolysis and hydrolysis products of $(CH_3)_2N(NH_2)_2Cl$
are discussed. The melting point of $(CH_3)_2N(NH_2)_2Cl$ has been corrected;
the new value is 124^OC with decomposition.

4. <u>Oxidation of 1,1-Dimethylhydrazine and Monomethylhydrazine by Oxygen</u>.

The study of the oxidation of 1,1-dimethylhydrazine in solutions in
diethyl ether or cyclohexane was carried out between 20 and 30^OC. The
principal product of this oxidation reaction under these conditions is
formaldehyde dimethylhydrazone. Among the other products identified were
water, 1,1,4,4-tetramethyl-2-tetrazene, nitrogen, methane, ammonia, formal-
dehyde monomethylhydrazone, sym. hexahydro-1,4-dimethyltetrazine, and
N-dimethylnitrosamine. At least fourteen other unidentified products were
detected by gas chromatography and mass spectral analysis. The rate of
reaction was followed by observing the change in concentration of 1,1-
dimethylhydrazine with respect to time. The data show that the reaction
is first order with respect to the hydrazine and the rate constats are of
the order of 10^{-6} sec^{-1}. The nature of the solvent does not have a large
effect on the reaction rate. The oxidation of monomethylhydrazine with
gaseous oxygen at or near room temperature was also studied and the follow-
ing principal products detected: methanol, sym. hexahydro-1,4-dimethyltetra-
zine, water, nitrogen, and methane. The first three of these were the
major oxidation products in the liquid phase. A mechanisms for this
oxidation is proposed.

5. Synthesis of Monomethylhydrazine in Non-Aqueous Solvents.

Virtually no reaction takes place between chloramine and methylamine in ether, xylene, methanol, or diglyme solutions. Monomethylhydrazine can, however, be synthesized in appreciable yield in various media when chloramination is carried out in the presence of a fixed base such as potassium hydroxide or sodium methoxide. Besides monomethylhydrazine, some of the oxidation products of monomethylhydrazine are also formed. These results are explained in terms of a possible mechanism involving the chloramide ion or imine diradical.

6. Formation of Dimethylmercury in the Oxidation of Monomethylhydrazine by Mercuric Oxide.

In an attempt to prepare symmetrical dimethyl-2-tetrazene by the oxidation of monomethylhydrazine with yellow mercuric oxide, a byproduct hitherto unreported for mercuric oxide oxidations of methyl substituted hydrazines, viz.; the highly toxic dimethylmercury, was obtained. It is suspected that this compound may be formed in the mercuric oxide oxidations of other methyl substituted hydrazines. Researchers should be aware of the considerable hazard associated with this possibility.

7. Reaction of Chloramine with Monomethylurea.

Preliminary investigations showed that chloramine, free of ammonia, dissolved in ether, reacts with an aqueous solution of monomethylurea to yield a complex mixture of monomethylhydrazine and its oxidation products, including the monomethylhydrazone of formaldehyde and methanol and other substances. 1,1-Dimethylhydrazine was also obtained. Similar results were obtained when an ethanol solution of ammonia-free chloramine was allowed

to react with an aqueous solution of monomethylurea.

Appendix   I

STUDIES OF THE CHLORAMINATION OF DIMETHYLAMINE
AND 1,1-DIMETHYLHYDRAZINE[1]

by

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Introduction

In an effort to find an alternative synthesis for 1,1-dimethyl-hydrazine, the reaction of chloramine with dimethylamine reported by Sisler et al more than two decades ago[2-21], has been the object of study in several laboratories. Several by-products of the chloramination of dimethylamine have been reported including 2,2-dimethyltriazanium chloride[15,22] and 1,1,4,4-tetramethyl-2-tetrazene[18,23]. In addition, the research reported herein will show that the dimethylhydrazone of formaldehyde is also a major product. This substance has been previously reported[24] as an oxidation product of 1,1-dimethylhydrazine, but had not previously been reported for the chloramination of dimethylamine. Since the formation of these by-products is deleterious with respect to the use of this reaction as the basis for a process for the manufacturing of 1,1-dimethylhydrazine, it is important to minimize by-product formation. The object of this research was to investigate in some detail the chloramination of dimethyamine, and particularly to determine the mechanism for the formation of the dimethylhydrazone of formaldehyde.

Materials. Chloramine was prepared by gas-phase reaction of ammonia[2] with chlorine and was either collected in cold, anhydrous ether or was reacted directly with $(CH_3)_2NH$ in a suitable solvent. When required, ammonia was removed from the chloramine by passing the ethereal solution of chloramine through a column of anhydrous copper (II) sulfate prior to reaction. The chloramine content of the solution was estimated either by addition of an aliquot portion of the solution to potassium iodide solution in 1 N acetic acid and subsequent titration of the released iodine

with standard thiosulfate solution before the experiment, or was determined by measuring the total chloride formed in the reaction at the end of the experiment using the Volhard Method. Dimethylamine was supplied by Matheson Gas Products and 1,1-dimethylhydrazine was obtained from the Naval Surface Weapons Center White Oak Laboratory. Dimethylhydrazine was refluxed and distilled over KOH before use. 1,1,4,4-Tetramethyl-2-tetrazene[18,23], and the dimethylhydrazone of formaldehyde[24] were prepared by methods reported in the literature. Diphenyldiazomethane and the diphenylhydrazone of formal- dehyde were prepared by methods reported in the literature[25,26]. These compounds were analyzed by gas chromatographic and nuclear magnetic resonance analyses to ascertain their purity. The solvents and other reagents used in this study were reagent grade and were dried, distilled and stored over appropriate drying reagents when desired.

Spectra. The nmr spectra of $CDCl_3$ or $(CD_3)_2SO$ solutions of samples were recorded on a Varian Model A-60-A NMR spectrometer. Tetramethylsilane and the sodium salt of 3-trimethylsilvlpropane sulfonic acid were used as internal standards in the two solvents, respectively. The infrared spectra of the solid samples in pressed KBr pellets and liquid samples placed between KBr plates were recorded on a Beckman IR-10 spectrometer.

Analysis. Perkin Elmer Model 810 and Varian Model 3700 gas chromato- graphs equipped with thermal conductivity detectors were used for the analyses of the various reaction products. The Carbowax colums of various lengths and internal diameters having 10% Carbowax + 5% KOH were used for the analysis of the liquid products and a molecular sieve 5-B 6 ft. x 1/8" column was used for the analysis of the gaseous reaction products. Helium

was used as the carrier gas and toluene was used as the internal standard
(when required) to relate the peak areas to the percent of the compounds
of interest. 1,1-Dimethylhydrazine in the reaction mixture was estimated
by titrating the solution acidified with aqueous hydrogen chloride with
0.025 M KIO_3 solution[27]. The melting points were determined on a Thomas-
Hoover capillary tube melting point apparatus and were reported uncorrected.
The elemental analyses were done by Galbraith Microanalytical Laboratories
in Knoxville, Tennessee.

Reaction of the Chloramine-Ammonia Mixture with Dimethylamine in
the Presence of KOH. In a typical experiment, dimethylamine (0.5 mole)
was condensed into a reaction vessel at Dry Ice-acetone temperature. To
this a precooled solution of potassium hydroxide (0.2 mole) in 150 ml. n-
butanol was added. The exit of the reaction vessel was connected to a dry
ice-acetone condenser and the mixture treated wtih NH_2Cl-NH_3 effluent of
the chloramine generator at room temperature for one hour. After the
chloramination, the reaction mixture was allowed to stand at room tempera-
ture to allow volatile gases to escape . The solids formed were filtered
out and the solution was fractionated on a spinning band column under an
atmosphere of nitrogen. The liquid distilling in the range 85-90°, was
collected and examined. The gas chromatograph of the sample showed a total
of 13 peaks. The major components which could be readily identified were
dimethylamine, 1,1-dimethylhydrazine, the dimethylhydrazone of formaldehyde,
water, 1,1,4,4-tetramethyl-2-tetrazene and butanol. The proton nmr spectrum
of the mixture also supported the presence of these components. The remaining
six components are in minute amounts constituting a total of 1.3% of the

mixture. The actual amount of 1,1-dimethylhydrazine present in the distillate was estimated by employing the nmr technique. A calibration was obtained by plotting the nmr intensity of the CH_3-proton signal of $(CH_3)_2NNH_2$ in n-butanol for various known solutions. Using this method, the yield of $(CH_3)_2NNH_2$ was found to be about 30% based on the chloramine used.

The solid material was washed with ether several times and dried under vacuum. It gave no signal in the proton nmr spectrum and does not melt up to $300^\circ C$. From the qualitative analysis it was identified as KCl.

Reaction of Chloramine with 1,1-Dimethylhydrazine. The apparatus used in this study consisted of a two-necked, 300 ml. reaction flask, a cold trap (Dry Ice-acetone), a source of helium supply, and a gas collector. The reaction flask was fitted with a magnetic stirring bar. One neck of the reaction flask was closed with a rubber septum. The other neck was connected through a glass "T" to the helium supply and the cold trap. The cold trap was then connected to the gas collector through a glass "T" and to a delivery tube. The remaining end of the glass "T" was closed with a rubber septum and was used as the sample withdrawal port. The entire apparatus (Fig. 1.) was flushed with helium gas until no nitrogen or oxygen was detectable by chromatographic analysis of the gas samples withdrawn through the sample withdrawal port. The helium flow was then stopped and the reaction flask was charged with 26.3 mmole of 1,1-dimethylhydrazine in 20 ml. of ether with a hyperdermic syringe and 120 ml. of ether solution containing 25.2 mmole of chloramine was added. The reaction mixture was stirred with a magnetic stirrer and the temperature was maintained at $20^\circ C$. After one hour, the total amount of gas collected was determined. Using

Figure 1
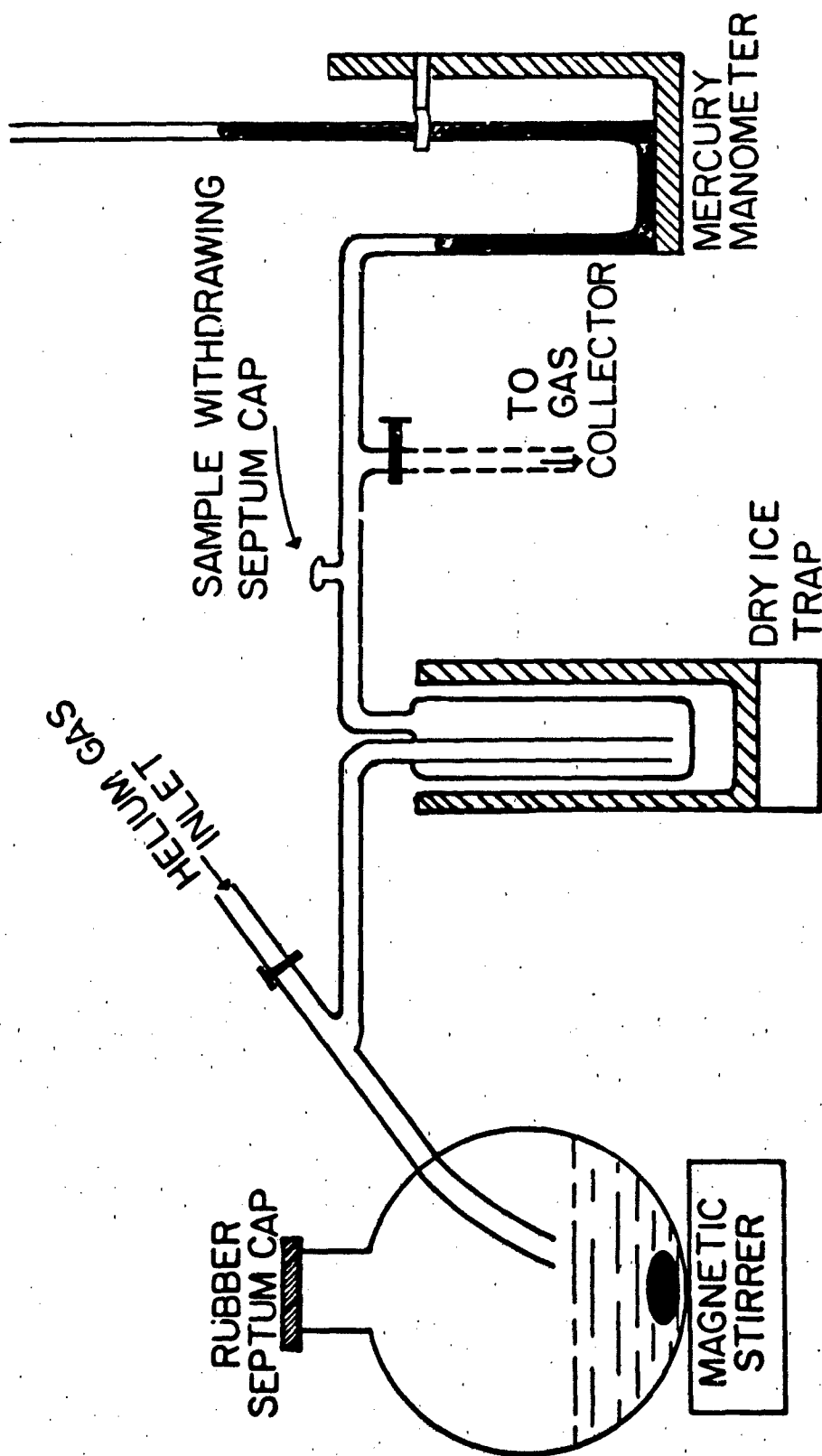
gas chromatographic analysis, the amounts of various components of the gas collected and the liquid in the reaction flask were found to be as follows: 1.53 mmole CH_4, 3.78 mmole N_2, 1.86 mmole $(CH_3)_2NN=CH_2$, 3.47 mmole 1,1,4,4-tetramethyl-2-tetrazene, and 0.15 mmole of $(CH_3)_2NNH_2$. In addition, 0.15 mmole of $[(CH_3)_2N(NH_2)_2]$ Cl was found in the solid, leaving a solid residue of 0.92 g.

Reaction of Mercuric Oxide (Yellow) with 1,1-Dimethylhydrazine. A two-necked flask was used for this study and all the reactants and products were kept under a dry nitrogen atmosphere. One neck of the flask was closed with a rubber septum cap and a glass bulb containing HgO was connected through a tygon tube to the other neck. Solutions of $(CH_3)_2NNH_2$ prepared in ether or in cyclohexane were injected in measured quantities into the reaction flask through the rubber septum cap while the temperature was maintained at $25^{\circ}C$. Small portions of yellow HgO were slowly added with constant stirring to the solutions of $(CH_3)_2NNH_2$. After the addition of the required amount of HgO, the reaction mixture was continuously stirred throughout the specified time period. The products of these reactions were then identified and estimated by liquid-gas chromatographic analysis and spectroscopic methods. The various reaction products obtained from the $(CH_3)_2NNH_2$-HgO reaction along with the reaction conditions are listed in Table I.

TABLE I

Product Analysis of the Reaction of 13.16 Mmole of

1,1-Dimethylhydrazine with 13.15 Mmole Mercury

Oxide (Yellow) at 25°C. in Diethyl Ether Solution

INITIAL $((CH_3)_2NNH_2)$	REACTION TIME HRS.	PER CENT PRODUCTS			TMT/FDMH RATIO
		UDMH	TMT	FDMH	
0.52 M	1 hr.	0.0	97.0	3.0	32.3
0.26 M	5 hrs.	Trace	92.3	8.7	10.5
0.13 M	18 hrs.	Trace	54.6	35.2	1.6
0.065 M	23 hrs.	Trace	25.2	44.8	0.55

UDMH = $(CH_3)_2NNH_2$

TMT = $(CH_3)_2NN=NN(CH_3)_2$

FDMH = $(CH_3)_2NN=CH_2$

Oxidation of 1,1-Dimethylhydrazine with Ag_2O. A solution of 13.16 mmole of $(CH_3)_2NNH_2$ in 25 ml. of diethyl ether was added to 3.05 g. (13.16 mmole) of Ag_2O and the reaction mixture was stirred for 30 minutes at room temperature. At the end of this time, the reaction products were analyzed by gas-liquid chromatography and were found to be $(CH_3)_2NNH_2$ 22%, $(CH_3)_2NN=CH_2$ 15% and $(CH_3)_2NN=NN(CH_3)_2$ 64%.

In a separate experiment 13.16 mmole of $(CH_3)_2NNH_2$ in 25 ml. of diethyl ether was added to 3.05 g. (13.16 mmole) of Ag_2O and the gaseous products were trapped and analyzed. The total amount of gas obtained was 5.50 mmole containing O_2 (air impurity, N_2, and CH_4.

Reaction of Phenyldiazomethane with Dimethyldiazene. Benzophenone hydrazone 3.87 g. (19.74 mmole) dissolved in 100 ml. of diethyl ether was treated with 5.03 g. (21.11 mmole) of Ag_2O and 2 g. of $MgSO_4$. Within three minutes of mixing the solution turned purple showing the formation of $(C_6H_5)_2CN_2$. The reaction mixture was kept in a water bath at 25^OC and stirred for 30 minutes. At the end of this period 1.0 ml. (.79 g.) of $(CH_3)_2NNH_2$ and 2 g. of $MgSO_4$ were added at once and then 3.35 g. (14.48 mmole) of Ag_2O was added in small portions over a 30 minute period. Gas evolution was observed but the solution remained purple in color and remained so even after all the Ag_2O was added. The solution was stirred for an additional 14 hours more, and was then filtered. To the filtrate a calculated amount of C_6H_5COOH was added and it was stirred for 8 hours. The purple color of solution changed to pale yellow color. The solution was then concentrated and the volume was reduced to 50 ml. It was extracted with 10% HCl solution. The HCl extract was treated with excess of NaOH at 0^OC and was extracted again with diethyl ether and over $MgSO_4$. The gas-liquid chromatographic analysis of this extract showed 7% $(CH_3)_2NN=CH_2$ and 93% $(CH_3)_2NN=NN(CH_3)_2$ plus diethyl ether.

The residue left after the HCl extraction was washed with 10% NaOH solution to remove excess of C_6H_5COOH. The solution was then saturated with NaCl, dried, and concentrated in vacuum over $MgSO_4$. The pale yellow solid recovered was washed with $NaHCO_3$ solution and extracted with ethyl alcohol and dried, yielding 3.54 g. of solid or 62% of the theoretical yield based on $(C_6H_5)_2C=N-NH_2$ taken. The solid was identified by its mp. (83.86^O observed vs. $88.-89^O$ literature) and its proton nmr spectra

(compared with Sadtta #12369) to be $C_6H_5COOCH(C_6H_5)_2$. Neither in the extract nor in the solid was

$$(CH_3)_2N-N=C \overset{\displaystyle C_6H_5}{\underset{\displaystyle C_6H_5}{\big<}}$$
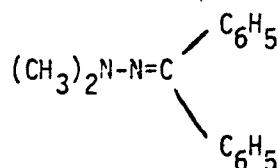
detected. Apparently, $(CH_3)_2\overset{+}{N}=\overset{-}{N}$ does not react with $(C_6H_5)_2CN_2$ to form benzophenone dimethylhydrazone.

Reactions of Silver Nitrate (Ag$_2$O) with Aqueous and Alkaline Solutions of 1,1-Dimethylhydrazine. Three different solutions of 1,1-dimethylhydrazine of compositions (1) 3.95 g. (65.8 mmole) $(CH_3)_2NNH_2$ in 100 ml. 2 M NaOH, (2) 3.95 g. $(CH_3)_2NNH_2$ in 100 ml. 5 M NaOH and (3) 3.95 g. $(CH_3)_2NNH_2$ in 100 ml. of 10 M NaOH were prepared in water. To the solution No. 1 50 ml. of silver nitrate solution containing 11.7 g. (69.1 mmole) of AgNO$_3$ was added and to the solutions No. 2 and 3 each of 75 ml. of silver nitrate solutions containing 22.4 g. (131.6 mmole) of AgNO$_3$ was added separately. The reaction mixtures were kept at room temperature and stirred. Two hours of reaction time was allowed in each case; the liquids in the reaction vessels were examined by gas chromatography. The identities of the various components were established by comparing their retention times with those of the known compounds and their quantities were determined by comparing the area intergals of the various peaks with standards. The per cent compositions of these reaction mixtures are listed in Table II.

TABLE II

Experiment No.	% Composition of Reaction Mixtures			
	UDMH	FDMH	TMT	CH_3OH
1. 2 M NaOH	52	17	16	15
2. 5 M NaOH	0	11	45	44
3. 10 M NaOH	0	6	12	82

Where UDMH is $(CH_3)_2NNH_2$; FDMH is $(CH_3)_2NN=CH_2$: and TMT is $(CH_3NN=NN(CH_3)_2$

It is important to note that increased concentration of OH^- cause a decrease in the formation of $(CH_3)_2NN=CH_2$ and an increased production of CH_3OH.

Results and Discussion

The results of the present investigation clearly establish the synthesis of $(CH_3)_2NNH_2$ by the reaction of chloramine with dimethylamine in non-aqueous solvents in the presence of a fixed base. However, besides the formation of $(CH_3)_2NNH_2$, several side products are also formed of which the major ones are the dimethylhydrazone of formaldehyde and tetramethyl-2-tetrazene. The formation of these two products in the reaction of $(CH_3)_2NNH_2$ and chloramine establishes clearly the fact that these side products obtained in the reaction of dimethylamine and chloramine are indeed the result of the further reaction of chloramine with $(CH_3)_2NNH_2$. It is interesting to note that both these products are also observed in the oxidation of dimethylhydrazine by gaseous oxygen[28] as well as by HgO.

It is therefore probable the dimethylhydrazone of formaldehyde and tetra-methyl-2-tetrazene are oxidation products of $(CH_3)_2NNH_2$ by chloramine. In addition to these, however, 2,2-dimethyltriazanium chloride is also formed as a reaction product of $(CH_3)_2NNH_2$ and chloramine[15,16]

In an earlier report[18] from this laboratory, the formation of tetra-methyl-2-tetrazene in the reaction of $(CH_3)_2NNH_2$ with chloramine was postu-lated to occur via the formation of the dimethyldiazine radical $(CH_3)_2\overset{+}{N}=\overset{-}{N}$. The mechanism of the formation of the dimethylhydrazone of formaldehyde as an oxidation product of $(CH_3)_2NNH_2$, is still uncertain.

Utvary and coworkers[29] have suggested that the first step in the mechanism for the formation of $(CH_3)_2NN=CH_2$ is the formation of dimethyldia-zene by the two-electron oxidation of $(CH_3)_2NNH_2$.

$$NH_2Cl + (CH_3)_2NNH_2 \longrightarrow (CH_3)\overset{+}{N}=\overset{-}{N}$$
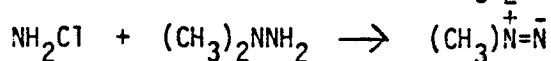
Utvary et al further proposed the following steps for the formation of $(CH_3)_2NN=CH_2$ from dimethyldiazine

$$(CH_3)_2\overset{+}{N}=\overset{-}{N} \longrightarrow CH_2N_2 + CH_4$$
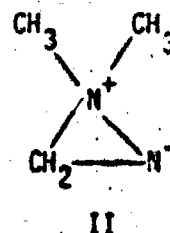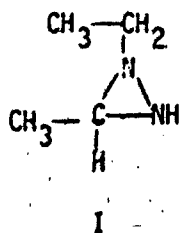

$$(CH_3)_2NN=CH_2 \longleftarrow$$
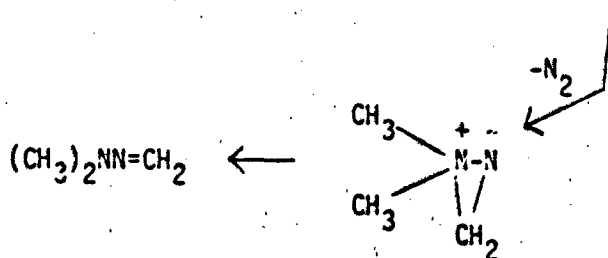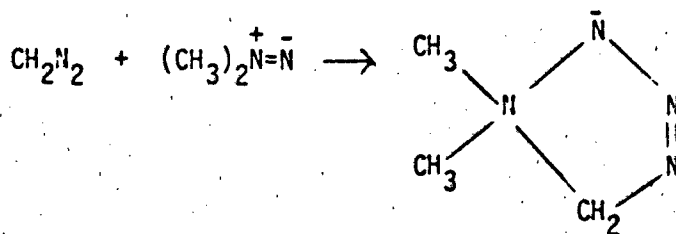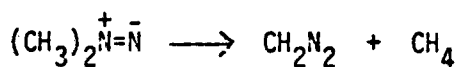
The study by Utvary et al was carried out in diethyl ether where the half life of the diazomethane is considerably greater than in alkaline aqueous solutions, with which it reacts rapidly. We have carried out our studies in water as well as in ether and have dmonstrated that $(CH_3)_2NN=CH_2$ is formed in aqueous solution as well as in ether. It is therefore unlikely that the mechanism involving diazomethane is the correct one.

In order to test the validity of Utvary mechanism, the diazene was generated from the $(CH_3)_2NNH_2$ and Ag_2O reaction in presence of excess of diphenyldiazomethane. If the Utvary mechanism were operative, the product arising from the trapping of the diazene with diphenyldiazomethane should be the dimethylhydrazone of benzophenone.

$$(C_6H_5)_2CN_2 + (CH_3)_2\overset{+}{N}=\overset{-}{N} \longrightarrow (CH_3)_2NN=C\overset{C_6H_5}{\underset{C_6H_5}{\Big\langle}} + N_2$$
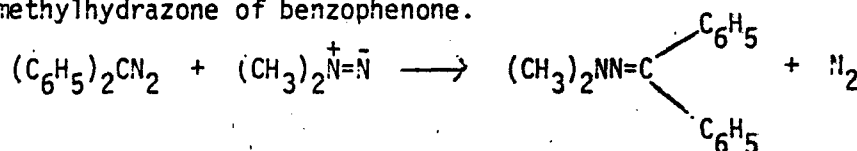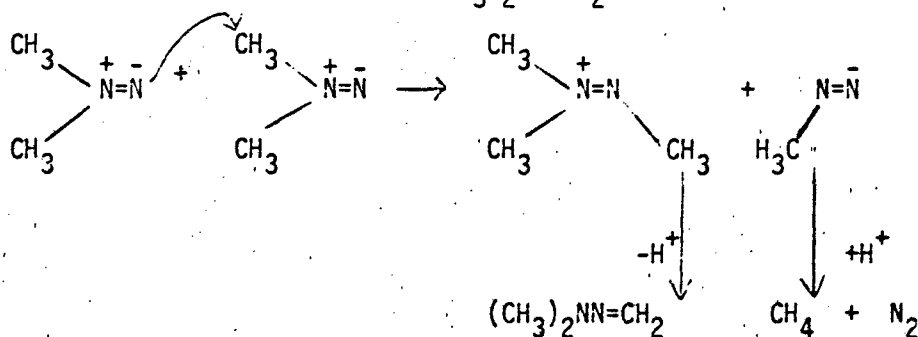
This compound was not found.

Other investigations reported in the literature cast more doubt on the Utvary mechanism. Lemal et al[30] synthesized the diaziridine (I) and subjected it to mild oxidizing conditions and isolated it unchanged. Utvary proposed that the intermediate (II) would be unstable towards oxidation and therefore change to $(CH_3)_2NN=CH_2$. This does not seem likely. The two compounds (I and II) are similar in structure and if (I) does not undergo oxidation, the probability of (II) being changed to $(CH_3)_2NN=CH_3$ is not great.

          I   II

It is reasonable to believe that the first step of the reaction for the formation of $(CH_3)_2NN=CH_2$ from the chloramination of $(CH_3)_2NNH_2$ is the formation of $(CH_3)_2\overset{+-}{NN}$ and we have shown that the methyl groups of this diazene are susceptible to nucleophilic attack. We have generated the diazine by reaction $(CH_3)_2NNH_2$ with Ag_2O and found that increasing the concentration of hydroxide ion increases the formation of methylalcohol (Table II) as shown by the following equation.

$$OH^- \quad CH_3 \atop OH^- \quad CH_3 \Big\rangle \overset{+}{N}=\overset{-}{N} \longrightarrow 2CH_3OH + N_2$$
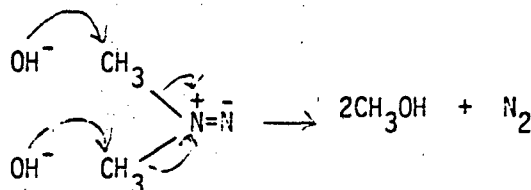
We propose that the formation of $(CH_3)_2NN=CH_2$ occurs by the following steps:

$$\begin{matrix} CH_3 \\ \diagdown \\ CH_3 \end{matrix} \overset{+}{N}=\overset{-}{N} \quad + \quad \begin{matrix} CH_3 \\ \diagdown \\ CH_3 \end{matrix} \overset{+}{N}=\overset{-}{N} \longrightarrow \begin{matrix} CH_3 \\ \diagdown \\ CH_3 \end{matrix} \overset{+}{N}=N \diagdown CH_3 \quad + \quad N=\overset{-}{N} \diagdown H_3C$$

$$-H^+ \downarrow \qquad\qquad +H^+ \downarrow$$

$$(CH_3)_2NN=CH_2 \qquad\qquad CH_4 + N_2$$

Since CH_4 and N_2 are formed in the same step the ratio CH_4/N_2 according to our proposed mechanism should be exactly 1.0. Our observed ratio of CH_4 to N_2 is 0.5. It does not, however, argue against our proposed mechanism since extra nitrogen would certainly arise from the secondary reaction of chloramine with the other reaction products initially formed from the $(CH_3)_2NNH_2$-NH_2Cl reaction, and would reduce the observed CH_4/N_2 ratio.

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Chloramination of Trimethylhydrazine

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The reaction of chloramine with trimethylhydrazine, $(CH_3)_2NNH(CH_3)$. has been investigated. The principal product formed when this reaction is carried out in ether is the dimethylhydrazone of formaldehyde, $(CH_3)_2NN=CH_2$. The absence of 1,2,2-trimethyltriazanium chloride, the expected product, is explained in terms of the weaker nucleophilicity of trimethylhydrazine compared to that of 1,1-dimethylhydrazine, which reacts with chloramine to form 2,2-dimethyltriazanium chloride. $[(CH_3)_2N^+(NH_2)_2]Cl$. The principal product of the chloramination of trimethylhydrazine, when the reaction is carried out in acetonitrile, is 2,2-dimethyltriazanium chloride. Mechanisms are proposed for the chloraminations in both solvents. Chloraminations of the dimethylhydrazone of formaldehyde and of tetramethyl-2-tetrazene, $(CH_3)_2NN=NN(CH_3)_2$, carried out for purposes of comparison, also resulted in formation of some 2,2-dimethyltriazanium chloride. Attempts to synthesize 1,1,2-trialkyltriazanium chlorides by reaction of 2,2-dimethyltriazanium chloride with alkyl halides were unsuccessful, resulting either in no reaction or in the formation of 2,2-dimethyltriazanium iodide. A mechanism for the formation of 2,2-dimethyltriazanium chloride by the chloramination of trimethylhydrazine is proposed.

The chemistry of 2,2-dialkyltriazanium salts, compounds of interest because they contain the $-N-N-N-$ chain and yet are stable at ordinary temperatures, has been discussed extensively in previous publications.[1-7] The chlorides can be most conveniently prepared by the reaction of chloramine with 1,1-dialkylhydrazines[2,3] or with secondary amines.[7] In a previous paper,[1] in which we reported the determination of the crystal structure of 2,2-dimethyltriazanium chloride, $[(CH_3)_2N(NH_2)_2]Cl$, and 1,1,1-trimethylhydrazinium chloride, $[(CH_3)_3NNH_2]Cl$, we suggested that the stability of 2,2-dialkyltriazanium salts is a result of the quaternization of the central nitrogen.

It seems reasonable to expect that 1,2,2-trialkyltriazanium salts would similarly be stable and could be prepared by the chloramination of trialkylhydrazines. However, Kren[8] isolated 2,2-dimethyltriazanium chloride instead of the expected 1,2,2-trimethyltriazanium chloride $[(CH_3)_2N(NH_2)(NHC-H_3)]Cl$ from the solid portion of the trimethylhydrazine-chloramination reaction mixture.

We have continued the investigation of the chloramination of trimethylhydrazine in order to identify other products, to formulate a reaction mechanism, and to determine possible reasons for the formation of 2,2-dimethyltriazanium chloride and the absence of 1,2,2-trimethyltriazanium chloride.

Experimental Section

Spectra. Infrared spectra of solid samples in pressed KBr pellets and liquid samples placed between KBr plates were recorded on a Beckman IR-10 spectrometer. Nuclear magnetic resonance spectra of $CDCl_3$ or Me_2SO-d_6 solutions of samples were recorded on a Varian Model A-60A NMR spectrometer at 40 °C. Tetramethylsilane and the sodium salt of 3-trimethylsilylpropanesulfonic acid were used as internal standards in the respective solvents.

Analyses. A Perkin-Elmer Model 820 gas chromatograph equipped with twin 12-ft 15% Carbowax columns was used for gas-liquid chromatography. An internal standard was used to relate peak areas to percents of compounds of interest.[9] Melting points were determined on a Thomas-Hoover capillary tube melting point apparatus. Elemental analyses were done by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Materials. Trimethylhydrazine. $(CH_3)_2NNH(CH_3)$,[10] tetramethyl-2-tetrazene,[11] $(CH_3)_2NN=NN(CH_3)_2$, and the dimethylhydrazone of formaldehyde,[10] $(CH_3)_2NN=CH_2$, were prepared by methods found in the literature. Prior to chloramination, these compounds were analyzed by gas-liquid chromatography and nuclear magnetic resonance spectroscopy to ascertain that they were free of contaminants, especially 1,1-dimethylhydrazine. Nuclear magnetic resonance spectral peaks for products and reactants in this study are listed in Table I. A sample of 2,2-dimethyltriazanium chloride prepared for our previous study[1] was also used in this study. Anal. Calcd for $C_2H_{10}N_3Cl$: C, 21.52; H, 8.97; N, 37.62. Found: C, 21.62;

H, 8.96; N, 37.50. Chloramine was produced in a Sisler-Mattair generator[12] by the gas-phase reaction of ammonia and chlorine. The rate of formation of chloramine was ca. 0.08 mol of NH_2Cl/h. All other reagents and solvents were obtained from commercial sources and were used without further purification.

Reactions on the Chloramine Generator. The general procedure is given here. Details for specific reactions are listed in Table II. The chloramine-ammonia generator effluent was bubbled through a solution of the reactant at room temperature. After completion of chloramination, the reaction mixture was allowed to stand in a flask protected from moisture by a Drierite-filled drying tube. After 24 h, the solid which had formed was separated from the solution by filtration.

Preparation of Ammonia-Free Chloramine. The generator effluent was bubbled through 1 L of dry ether for 2 h. The mixture was then allowed to stand overnight after which the volume of solvent was reduced by passing a stream of nitrogen over the solution until the desired chloramine concentration was obtained (ca. 0.2 M). The chloramine concentration was determined by addition of an aliquot of the chloramine solution to an acidic potassium iodide solution followed by titration of the liberated iodine with a standard sodium thiosulfate solution. This chloramine solution is relatively stable; it can be stored for days without appreciable decomposition of chloramine. The last traces of ammonia were removed by pouring the chloramine solution through a column packed with anhydrous copper sulfate.[13]

Other Chloraminations of Trimethylhydrazine (See Table II for Details). Trimethylhydrazine, dissolved in ether, was placed into a nitrogen-swept three-necked flask equipped with a condenser, mechanical stirrer, and a pressure-equalized dropping funnel. Ethereal chloramine, either in ammonia-free form or in the stable solution described above, was added dropwise with stirring. After addition was complete, stirring was continued for 3 h after which time all of the chloramine had reacted. The reaction mixture was then filtered.

Reaction of Ammonia-Free Chloramine with Trimethylhydrazine in Acetonitrile. Ammonia-free chloramine (35 mmol dissolved in 130 mL of ether) was mixed with 200 mL of acetonitrile in a nitrogen-swept flask cooled in an ice bath. Trimethylhydrazine, 0.3 mL (31 mmol) in 100 mL of acetonitrile, was added dropwise with stirring. A white solid began forming immediately. Stirring was continued for 2 h after addition of trimethylhydrazine was complete; the mixture was then allowed to stand overnight. The white solid, collected by filtration, was found to consist entirely of ammonium chloride. The solvent was removed from the filtrate under reduced pressure leaving a small amount of an oily residue which could not be further characterized.

Identification of 2,2-Dimethyltriazanium Chloride. After each mixture was filtered, the solid products were washed with ether and dried under vacuum. Samples of from 50 to 200 mg were dissolved in 1 M sulfuric acid and titrated iodometrically[14] to determine the amount of triazanium salts present (1 mol of triazanium ions oxidizes 2 mol of iodide). Ammonium chloride, identified by its infrared spectrum, was the only solid product formed in reactions where ammonia-free solutions of chloramine were added dropwise to ethereal trimethylhydrazine.

Table I. Nuclear Magnetic Resonance Spectral Peaks of Reactants and Products of This Study

	Solvent	τ peak 1, ppm	τ peak 2, ppm	Ratio of peak areas: 1/2
2.2-Dimethyltriazanium chloride, [(CH$_3$)$_2$N$^+$(NH$_2$)$_2$]Cl$^-$	Me$_2$SO-d$_6$	3.23 (NH$_2$)	6.43 (CH$_3$)	4/6
2.2-Dimethyltriazanium iodide, [(CH$_3$)$_2$N$^+$(NH$_2$)$_2$]I$^-$	Me$_2$SO-d$_6$	3.62 (NH$_2$)	6.42 (CH$_3$)	4/6
Dimethylhydrazone of formaldehyde, (CH$_3$)$_2$NN=CH$_2$	CDCl$_3$	3.17 (CH$_2$)	7.20 (CH$_3$)	2/6
Trimethylhydrazine, (CH$_3$)$_2$NNH(CH$_3$)	CDCl$_3$	7.48 (CH$_3$)	7.62 (CH$_3$)	3/6/(1)^a
Tetramethyl-2-tetrazene, (CH$_3$)$_2$NN=NN(CH$_3$)$_2$	CDCl$_3$	7.19 (CH$_3$)		

^{a} NH peak appears at τ 7.78 ppm.

Table II. Reaction Conditions and Amounts of Products Formed in Chloraminations

	Amt of reactant, mmol	Amt of NH$_2$Cl, mmol	Solvent	Products	Amt of product
Trimethylhydrazine	9	25^a	Ether	Dimethylhydrazone of formaldehyde	0.69 mol/mol of trimethylhydrazine
				2.2-Dimethyltriazanium chloride	0.09 mol/mol of NH$_2$Cl
Trimethylhydrazine	7	6^b	Ether	Dimethylhydrazone of formaldehyde	0.96 mol/mol of NH$_2$Cl
Trimethylhydrazine	23	16^c	Ether	Dimethylhydrazone of formaldehyde	0.62 mol/mol of NH$_2$Cl
Trimethylhydrazine	9	25^a	Acetonitrile	2.2-Dimethyltriazanium chloride	0.66 mol/mol of trimethylhydrazine
Dimethylhydrazone of formaldehyde	23	50^a	Ether	2.2-Dimethyltriazanium chloride	0.11 mol/mol of dimethylhydrazone
Dimethylhydrazone of formaldehyde	23	50^a	Acetonitrile	2.2-Dimethyltriazanium chloride	0.09 mol/mol of dimethylhydrazone
Tetramethyl-2-tetrazene	8	25^a	Acetonitrile	2.2-Dimethyltriazanium chloride	0.64 mol/mol of tetramethyl-2-tetrazene

^{a} Generator effluent bubbled through solution of reactant. ^{b} Chloramine, in stable solution not made ammonia-free, added dropwise to ethereal trimethylhydrazine. ^{c} Ammonia-free chloramine added dropwise to ethereal trimethylhydrazine.

The solids which contained triazanium ions were extracted into boiling 3:1 acetone:ethanol mixtures. When the solutions had cooled, ether was added to reprecipitate the extracted materials which were collected by filtration. These solids were all identified as 2.2-dimethyltriazanium chloride by their infrared and NMR spectra and melting points which were identical with those of an authentic sample of 2.2-dimethyltriazanium chloride. The nonextractable solid remaining was identified as ammonium chloride.

Identification of the Dimethylhydrazone of Formaldehyde. After chloramination had been completed, aliquots of the ethereal solutions from the trimethylhydrazine-chloramine reactions were analyzed by gas-liquid chromatography to determine products present. The only peak found in each chromatogram (in addition to that of unreacted trimethylhydrazine) appeared at the retention time expected for the peak of the dimethylhydrazone of formaldehyde. An authentic sample of the latter compound added to these solutions caused the area of this peak to increase. After the solids were removed by filtration, enough ether was distilled from each solution to reduce the volume to ca. 10 mL, the infrared spectrum of this solution was found to contain a peak at 1585 cm^{-1} characteristic of the C=N stretch of the dimethylhydrazone of formaldehyde[15] and the NMR spectrum of this solution contained peaks consistent with those found in the NMR spectrum of the dimethylhydrazone of formaldehyde.
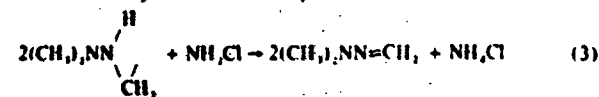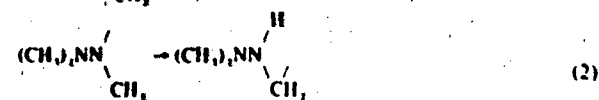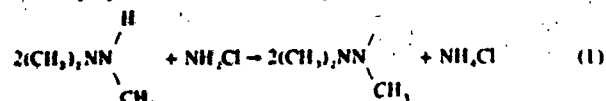
Reactions of 2.2-Dimethyltriazanium Chloride with Alkylating Agents. 2.2-Dimethyltriazanium chloride, 0.45 g (4.0 mmol), was dissolved in 15 mL of absolute ethanol in a nitrogen-swept flask equipped with a magnetic stirrer and a reflux condenser. After 3 mL of methyl iodide was added, the solution was refluxed for 1 h. After the solution had cooled, ether was added to precipitate the solid product. This solid was collected by filtration and recrystallized from a 3:1 acetone:ethanol mixture. Anal. Calcd for C$_3$H$_{10}$N$_3$I: C, 11.82; H, 4.93; N, 20.69. Found: C, 11.82; H, 4.96; N, 20.69. Melting points: lit. for 2.2-dimethyltriazanium iodide, 181 °C dec; found, 169-170 °C dec.

Under the same conditions 2.2-d methyltriazanium iodide was the only triazanium salt obtained from the reaction of 2.2-dimethyltriazanium chloride with ethyl iodide. Attempts to react 2.2-di-

methyltriazanium chloride with ethyl bromide under the same conditions were successful; the starting material was recovered unchanged.

Results and Discussion

The principal product of all three reactions of trimethylhydrazine with chloramine in ether was the dimethylhydrazone of formaldehyde and ammonium chloride. It is not certain whether the small amount of 2.2-dimethyltriazanium chloride, 0.09 mol/mol of trimethylhydrazine, formed in the reaction run on the generator, is a product of the chloramination of trimethylhydrazine or of the dimethylhydrazone of formaldehyde. Chloramination of the latter compound in ether also resulted in formation of small amounts of 2.2-dimethyltriazanium chloride, 0.11 mol/mol of dimethylhydrazone. The following mechanism is proposed for the formation of the dimethylhydrazone of formaldehyde from trimethylhydrazine:

$$2(CH_3)_2NN \begin{array}{c} H \\ / \\ \backslash \\ CH_3 \end{array} + NH_2Cl \rightarrow 2(CH_3)_2NN \begin{array}{c} / \\ \backslash \\ CH_2 \end{array} + NH_4Cl \quad (1)$$

$$(CH_3)_2NN \begin{array}{c} H \\ / \\ \backslash \\ CH_2 \end{array} \rightarrow (CH_3)_2NN \begin{array}{c} / \\ \backslash \\ CH_2 \end{array} \quad (2)$$

$$2(CH_3)_2NN \begin{array}{c} H \\ / \\ \backslash \\ CH_2 \end{array} + NH_2Cl \rightarrow 2(CH_3)_2NN=CH_2 + NH_4Cl \quad (3)$$

Steps 1 and 3 are considered reasonable because abstractions of amino hydrogens by chloramine are well-known. For example, tetramethyl-2-tetrazene, also a product of the chloramination of 1.1-dimethylhydrazine, is believed[14] to be formed by the coupling of two molecules of (CH$_3$)$_2$N—N

which are formed through the abstraction of the amino hydrogens of 1,1-dimethylhydrazine by chloramine. The transfer shown in step 2 of a hydrogen atom from the carbon to the adjacent nitrogen is postulated on the ability of amino radicals to abstract hydrogen atoms from carbons. For example, it has been shown that amino radicals abstract hydrogens from olefins rather than adding to double bonds.[16]

In contrast to the chloramination of trimethylhydrazine, good yields of products of both nucleophilic substitution (2,2-dimethyltriazanium chloride) and hydrogen abstraction (tetramethyl-2-tetrazene) can be obtained by chloramination of 1,1-dimethylhydrazine[14] in ether which indicates that the two reactions occur at comparable rates. The absence of 1,2,2-trimethyltriazanium chloride, the expected substitution product, is evidence that the rate of nucleophilic substitution of trimethylhydrazine or chloramine in ether is much slower than the rate of abstraction of the amino hydrogen. We believe that the rate of substitution of chloramine is slower for trimethylhydrazine than for 1,1-dimethylhydrazine because trimethylhydrazine is a weaker nucleophile. Although nucleophilicities of these compounds have not been measured, trimethylhydrazine is a weaker base than 1,1-dimethylhydrazine (pK's are 6.79 and 7.44, respectively).[17] Relative basicity is not a reliable measure of relative nucleophilicity in cases where a less basic atom is more polarizable than a more basic one or where the more basic atom is more sterically hindered. However, it is reasonable to assume that the greater basicity of 1,1-dimethylhydrazine is evidence of greater nucleophilicity because polarizabilities of the two compounds are likely to be similar and because trimethylhydrazine, the compound with more steric crowding, is the weaker base.

Trimethylhydrazine was chloraminated in acetonitrile to determine whether there would be changes in reaction products if chloramination occurred in a more polar solvent. When trimethylhydrazine in acetonitrile was treated with the ammonia-chloramine effluent from the generator, the major product formed was 2,2-dimethyltriazanium chloride, the amount of 2,2-dimethyltriazanium chloride produced being much greater than when trimethylhydrazine is chloraminated in ether, 0.66 mol/mol of trimethylhydrazine compared with 0.09 mol/mol of trimethylhydrazine, respectively. In contrast, the yield of 2,2-dimethyltriazanium chloride obtained from the chloramination of the dimethylhydrazine of formaldehyde remains essentially unchanged regardless of whether the dimethylhydrazone of formaldehyde is chloraminated in ether or in acetonitrile (0.09 mol/mol of dimethylhydrazone and 0.11 mol/mol of dimethylhydrazone, respectively).
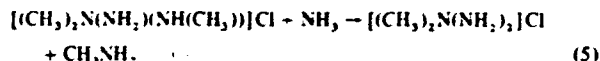
The formation of 2,2-dimethyltriazanium chloride from trimethylhydrazine in acetonitrile must proceed through formation of an intermediate product followed by reaction of this intermediate with chloramine or ammonia. The higher yield of 2,2-dimethyltriazanium chloride resulting from chloramination of trimethylhydrazine than from chloramination of the dimethylhydrazone of formaldehyde in acetonitrile implies that the intermediate is mostly, if not entirely, a species other than the dimethylhydrazone of formaldehyde.

According to Utvary,[18] 2,2-dimethyltriazanium chloride is also formed by the reaction in ether of a chloramine-ammonia mixture with tetramethyl-2-tetrazene. In order to consider the possibility that tetramethyl-2-tetrazene is the intermediate in the chloramination of trimethylhydrazine in acetonitrile, tetramethyl-2-tetrazene in acetonitrile was chloraminated with the generator effluent. The amount of 2,2-dimethyltriazanium chloride found, 0.64 mol/mol of tetramethyl-2-tetrazene, is approximately half the amount found when trimethylhydrazine is chloraminated since 2 mol of trimethylhydrazine would be required to form 1 mol of tetramethyl-2-tetrazene. Therefore,

it is reasonable to assume that the intermediate in the formation of 2,2-dimethyltriazanium chloride from trimethylhydrazine is not tetramethyl-2-tetrazene.

In an attempt to isolate the intermediate in this reaction, trimethylhydrazine was allowed to react with ammonia-free chloramine in acetonitrile. No 2,2-dimethyltriazanium chloride was found. The absence of 2,2-dimethyltriazanium chloride from the ammonia-free reaction is evidence that ammonia is necessary for the formation of 2,2-dimethyltriazanium chloride.

A feasible, although speculative, mechanism for the formation of 2,2-dimethyltriazanium chloride from the chloramination of trimethylhydrazine in acetonitrile in the presence of ammonia can be postulated which involves the formation of 1,2,2-trimethyltriazanium chloride followed by transamination.

$$(CH_3)_2NNH(CH_3) + NH_2Cl \rightarrow [(CH_3)_2N(NH_2)(NH(CH_3))]Cl \qquad (4)$$

$$[(CH_3)_2N(NH_2)(NH(CH_3))]Cl + NH_3 \rightarrow [(CH_3)_2N(NH_2)_2]Cl$$
$$+ CH_3NH_2 \qquad (5)$$

Nucleophilic substitution followed by transamination has been suggested as a mechanism for the formation of 2,2-dimethyltriazanium chloride from the reaction of 2-dimethylamino-1,3,2-dioxophospholane with the chloramine-ammonia generator effluent.[19]

Reaction of 2,2-Dimethyltriazanium Chloride with Alkylating Agents

We unsuccessfully attempted to prepare 1,1,2-trialkyltriazanium salts by alkylation of 2,2-dimethyltriazanium chloride using methyl and ethyl bromide both at room and at elevated temperatures. At room temperature no reaction occurred and the 2,2-dimethyltriazanium chloride was recovered unchanged. Refluxing an ethanolic solution of ethyl bromide and 2,2-dimethyltriazanium chloride also did not effect any reaction; refluxing 2,2-dimethyltriazanium chloride with methyl and ethyl iodide resulted in formation of 2,2-dimethyltriazanium iodide. This compound has been previously prepared by adding potassium iodide to 2,2-dimethyltriazanium chloride in liquid ammonia.[5]

The inertness of the terminal nitrogens of 2,2-dimethyltriazanium chloride toward alkylation by alkyl halides is also characteristic of terminal nitrogens in quaternary hydrazinium salts. For example, methyl iodide does not alkylate 1,1,1-trimethylhydrazinium iodides: no reaction occurs except under extreme conditions where the hydrazinium salt decomposes.[20]

Although the attempt to react 2,2-dimethyltriazanium chloride with alkyl halides did not result in alkylation at the terminal nitrogens, it did further point out the previously discussed[1] resemblance of 2,2-dialkyltriazanium salts to 1,1,1-trialkylhydrazinium salts.

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Pyrolysis and Hydrolysis of 2,2-Dimethyltriazanium Chloride

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The purification, hydrolysis, and pyrolysis of 2,2-dimethyltriazanium chloride are discussed. The gas chromatography data indicate that the pyrolysis products in a helium atmosphere are NH_4Cl, N_2, $(CH_3)_2NN=CH_2$, and small amounts of $(CH_3)_2NNH_2$ and $(CH_3)_2NN=NN(CH_3)_2$. Under vacuum, with or without solid NaOH, the products are NH_4Cl, N_2, $(CH_3)_2NN=CH_2$, and trace amounts of $(CH_3)_2NN=NN(CH_3)_2$, but no $(CH_3)_2NNH_2$. The ultraviolet spectroscopy data for the hydrolysate of $(CH_3)_2N(NH_2)_2Cl$ in 0.5–2.0 N KOH solution indicate that $(CH_3)_2NN=CH_2$ is the major product. The value of λ_{max} for $(CH_3)_2NN=CH_2$ is pH dependent and shifts toward shorter wavelengths with increased pH. The rate of formation of $(CH_3)_2NN=CH_2$ follows approximately first-order kinetics with respect to $(CH_3)_2N(NH_2)_2Cl$. The mechanisms for the formation of various pyrolysis and hydrolysis products of $(CH_3)_2N(NH_2)_2Cl$ are discussed. The melting point of $(CH_3)_2N(NH_2)_2Cl$ has been corrected; the new value is 124 °C with decomposition.

Introduction

One potential process for the synthesis of 1,1-dimethylhydrazine is the liquid-phase[1-3] chloramination of dimethylamine. One of the byproducts of the chloramination is 2,2-dimethyltriazanium chloride,[4-9] [$(CH_3)_2N(NH_2)_2$]Cl. It has been shown that the latter substance is formed by the reaction between the 1,1-dimethylhydrazine and chloramine.[10-13]

Giordano and Sisler[14] have also obtained dimethyltriazanium chloride by the chloramination of trimethylhydrazine. Dimethyltriazanium chloride is reported to be stable in air and in neutral aqueous solutions.[15] It can be recrystallized[10] from boiling ethanol, acetone, diethyl ether, or acetonitrile. In a recent report Giordano, Palenik, and Sisler[16] have shown the structure of 2,2-dimethyltriazanium chloride to be

$$
\left[\begin{array}{c} CH_3 \quad\quad NH_2 \\ \diagdown\quad/ \\ N \\ /\quad\diagdown \\ CH_3 \quad\quad NH_2 \end{array} \right]^+ Cl^-
$$
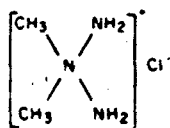
analogous to the structure of [$N(CH_3)_4$]Cl.

Although 2,2-dimethyltriazanium chloride is among the first known stable alkyl compounds which contain a single bonded chain of more than two nitrogen atoms, it is an undesirable byproduct in the synthesis of unsymmetrical dimethylhydrazine, $(CH_3)_2NNH_2$, by chloramination of dimethylamine. It was, therefore, the object of this study to determine the thermal and hydrolytic stabilities of 2,2-dimethyltriazanium chloride, to determine the various products formed by its pyrolysis and hydrolysis, and to determine the reaction mechanisms for the formation of the various products from the pyrolysis or hydrolysis. This information would be useful in optimizing the yield of unsymmetrical dimethylhydrazine from the chloramination of dimethylamine.

Experimental Section

Materials. The 2,2-dimethyltriazanium chloride used in this study was prepared and purified by procedures described in the literature.[10,11,14] Its ¹H NMR spectrum showed ammonium chloride as

an impurity although its melting point agreed with that reported in literature.[10,11] It was, therefore, further purified by dissolving 0.731 g in 30 mL of anhydrous ethanol at room temperature and recrystallizing it by adding an acetone–ether mixture (90 mL of acetone, 300 mL of ether) at −4 °C. The material obtained by this procedure melted at 124 °C (with decomposition) and showed no ammonium chloride impurity in its ¹H NMR spectrum or its infrared spectrum. The dimethylhydrazones of formaldehyde[17] ($(CH_3)_2NN=CH_2$) and tetramethyl-2-tetrazene[18] ($(CH_3)_2NN=NN(CH_3)_2$) were prepared by methods found in the literature. These compounds were analyzed by gas–liquid chromatography and nuclear magnetic resonance spectroscopy to ascertain that they were free from appreciable amounts of contaminants. Unsymmetrical dimethylhydrazine, $(CH_3)_2NNH_2$, of 95% purity was obtained from the Naval Surface Weapons Center, White Oak Laboratory. It was refluxed and distilled[11] over solid potassium hydroxide in a nitrogen atmosphere before use. The product so obtained invariably contained formaldehyde dimethylhydrazone. The amount of the hydrazone was determined and an appropriate correction was applied when it was necessary. Chloramine was prepared by the reaction of ammonia and chlorine in a nitrogen atmosphere in a gas phase reactor of the type described by Sisler and Mattair.[19] The chloramine content was determined[11] by shaking a measured sample with potassium iodide in 1 N acetic acid solution and titrating the liberated iodine with standard thiosulfate solution. The solvents used were dried and distilled over appropriate drying agents in a nitrogen atmosphere and were stored under dry conditions. The reagents and the buffers were ACS reagent grade and were used as supplied.

Spectra. Ultraviolet spectra were obtained with a Beckman DB spectrophotometer. A hydrogen lamp was used for wavelengths less than 340 nm and a tungsten lamp for the longer wavelengths. The measurements were made in matched quartz cells (with less than 1% of transmittance difference). The infrared spectra of solid samples (in pressed KBr pellets and liquid samples placed between KBr plates) were recorded with a Beckman IR-10 spectrometer. The ¹H NMR spectra of solutions of the samples in $CDCl_3$ or Me_2SO-d_6 were recorded with a Varian Model A-60 A NMR spectrometer using tetramethylsilane as an internal standard.

Analyses. All pH measurements were made with a Corning Model 12 Research pH meter using an Orion Model 91-01-00 pH electrode and Coleman Model 3-711 standard calomel reference electrode. The pH meter was standardized by using ACS grade buffers (pH 10.00 and 6.86) immediately before use. The instrument drift was less than 0.05 pH unit/h. A Perkin-Elmer Model 810 gas chromatograph equipped with twin 12 ft by ¹/₈ in. E-20 Carbowax KOH 5% columns and a thermal conductivity detector was used for gas–liquid chro-

Table I. Pyrolysis of [(CH$_3$)$_2$N(NH$_2$)$_2$]Cl between 135 and 600 °C

interface temp, °C	100	residue, %	41.9
sample wt, mg	4.3	He flow rate, mL min	27
residue wt, mg	1.8	column temp, °C	100

final temp, °C	pyrolysis interval, s	products
135	10	no product
150	10	no product
200	10	FDMH
225	10	N$_2$, UDMH,[b] FDMH,[c] unknown
250	10	N$_2$, UDMH, FDMH
275	10	N$_2$, FDMH
300	10	N$_2$, FDMH
350	10	N$_2$, UDMH, FDMH, unknown
400	10	N$_2$, UDMH, FDMH
500	5	N$_2$, ether,[a] UDMH, FDMH
600	2	no product

[a] Ether was used in the recrystallization of [(CH$_3$)$_2$N(NH$_2$)$_2$]Cl.
[b] UDMH = (CH$_3$)$_2$NNH$_2$. [c] FDMH = (CH$_3$)$_2$NN=CH$_2$.

matography. An internal standard was used to relate the peak areas to the percent of compounds of interest.[20] Helium was used as the carrier gas.

Pyrolysis of Dimethyltriazanium Chloride in a Helium Atmosphere. For the pyrolytic study of dimethyltriazanium chloride in a helium atmosphere a Pyroprobe-100 supplied by Chemical Data Systems was used. The Pyroprobe-100 is a solid-state pyrolyzer, which essentially consists of three major parts: the interface, the pyroprobe, and the electrical control system. The interface was mounted on the injector port of the gas chromatograph column where it became an extension of the injector port. The interface was also used as the pyroprobe holder. Since the carrier gas enters through the interface, the atmosphere inside the interface and the column was the same, viz., helium. The temperature of the interface was maintained at 100 °C. The pyroprobe used in this study had a platinum spiral sample holder with a probe seal and an extension cable connected to the electrical control system. The weighed samples of dimethyltriazanium chloride were placed in the platinum spiral on the pyroprobe. The pyroprobe was then inserted into the interface and sealed. The sample was allowed to stay in the interface for a minimum of 10 min to allow the air and moisture to be purged from the interface and the column. By use of the electrical control, the final pyrolysis temperature, the duration of pyrolysis, and the rate of reaching the final temperatures were adjusted as desired. At the desired time the run button was pressed to start the pyrolysis. The volatile pyrolysis products were carried into the analytical gas chromatograph column with the carrier gas and were identified by comparing their retention times with the retention times of the known substances. The weights of the solid
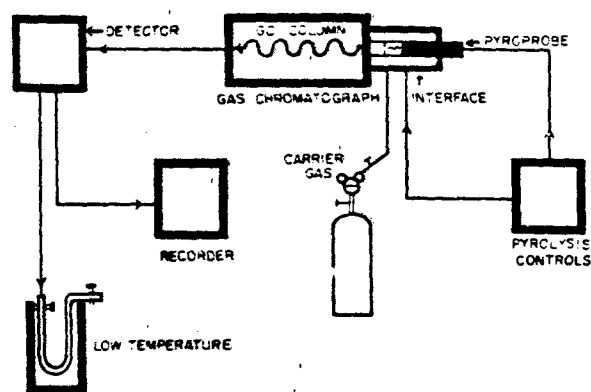

Figure 1. Schematics of the pyroprobe gas chromatograph system.

residues that remained in the sample tube, were determined and percentages of residue remaining were calculated. The solid residues were shown to be NH$_4$Cl by their infrared spectra.[21] The results of the pyrolysis of the same sample of dimethyltriazanium chloride between 135 and 600 °C are listed in Table I and the results of the pyrolysis of different samples of this substance at various temperatures are listed in Table II. The schematics of the pyroprobe and gas chromatograph system are shown in Figure 1.

Pyrolysis of Dimethyltriazanium Chloride under Vacuum. Known weights of solid 2,2-dimethyltriazanium chloride and solid NaOH were pyrolyzed through the temperature range 100–185 °C over a 30-min period and the volatile pyrolysis products condensed in a thoroughly degassed dry ether–toluene mixture (100 mg of toluene/100 mL of ether) cooled by liquid nitrogen. The ether–toluene solution of the pyrolysis products was then examined by gas chromatography. The pyrolysis products were identified by comparing their retention times with those of known substances under similar conditions. The various products and their quantities obtained are listed in Table III. A white residue remained in the reaction flask and was shown by its infrared spectrum to be ammonium chloride[21] when no sodium hydroxide was used. The pressure caused by the pyrolysis products generally dropped to half of its original value when the products were cooled to liquid-nitrogen temperature. Although the identities of the noncondensable gases were not determined in these experiments, we believe, on the basis of experimental results on the pyrolysis of dimethyltriazanium chloride in helium atmosphere, this gas to be nitrogen. Some products other than formaldehyde dimethylhydrazone and tetramethyltetrazene were detected in the gas chromatographic analysis; the identities of these were not established.

Hydrolysis of Dimethyltriazanium Chloride in Aqueous Base. For an estimation of the amount of formaldehyde dimethylhydrazone

Table II. Pyrolysis of [(CH$_3$)$_2$N(NH$_2$)$_2$]Cl at 350 and 400 °C

		interface temp, °C		100		column temp, °C		100
		He flow rate, mL/min		24				

sample wt, mg	residue wt, mg	% wt of residue	final temp, °C	interval times, s	products
5.5	2.8	50.9	350	2	N$_2$, CH$_4$, ether,[a] (CH$_3$)$_2$NNH$_2$, (CH$_3$)$_2$NN=CH$_2$, one unknown[b]
5.6	3.3	58.9	350	2	N$_2$, ether, (CH$_3$)$_2$NN=CH$_2$, and two unknowns
4.1	3.4	82.9	400	5	N$_2$, ether, (CH$_3$)$_2$NNH$_2$, (CH$_3$)$_2$NN=CH$_2$, (CH$_3$)$_2$NN=NN(CH$_3$)$_2$, and two unknowns
4.6	3.4	73.9	400	5	N$_2$, CH$_4$, ether, (CH$_3$)$_2$NNH$_2$, (CH$_3$)$_2$NN=CH$_2$, (CH$_3$)$_2$NN=NN(CH$_3$)$_2$, and two unknowns

[a] Ether was used for recrystallization. [b] One of the unknowns in substantial amount.

Table III. Pyrolysis Products of [(CH$_3$)$_2$N(NH$_2$)$_2$]Cl under Vacuum

mmol of [(CH$_3$)$_2$N(NH$_2$)$_2$]Cl	mol of NaOH/mol of [(CH$_3$)$_2$N(NH$_2$)$_2$]Cl	mmol of total (CH$_3$)$_2$NN=CH$_2$ formed	mmol of total (CH$_3$)$_2$NN=NN(CH$_3$)$_2$ formed
0.33	0	0.042	0.009
0.42	31.0	0.132	0.002
0.13	15.0	0.003	trace
0.22	1.8	0.048	0.009
0.28	300.0	0.053	0.003
0.23	11.0	0.057	0.030

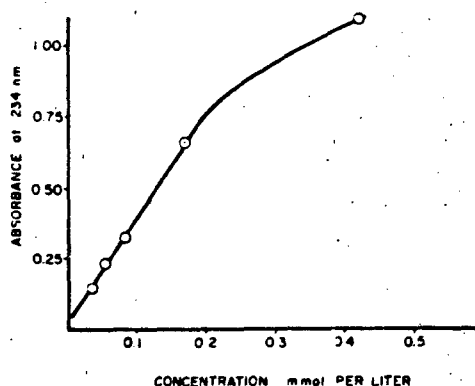**Figure 2.** Absorbance at wavelength 234 nm and near pH 13.8 vs. concentration of $(CH_3)_2NN=CH_2$.

Table IV. Hydrolysis of $[(CH_3)_2N(NH_2)_2]Cl$ in 1 N KOH as Function of $[(CH_3)_2N(NH_2)_2]Cl$ Concentration Determined by UV Spectrophotometry at 234 nm

mmol of $[(CH_3)_2N(NH_2)_2]Cl/L$	mmol of $(CH_3)_2NN=CH_2/L$
0.30	0.05
0.60	0.12
0.90	0.14
1.50	0.23
3.00	0.37

Table V. λ_{max} of $(CH_3)_2NN=CH_2$ and $[(CH_3)_2N(NH_2)_2]Cl$ Solutions as a Function of pH

solution	pH	λ_{max}
0.4×10^{-3} M FDMH[a] in 1 N KOH + 3.0 mL 5 N NaOH	13.90	230
0.4×10^{-4} M FDMH in 1 N KOH + 1.5 mL 5 N NaOH	13.89	235
0.4×10^{-4} M FDMH in 1 N KOH	13.75	238
0.4 mmol FDMH in 1 N KOH + HCl	11.40	240
DMTC[b] in 1 N KOH	13.79	234
DMTC in 1 N KOH + HCl	13.40	237
DMTC in 1 N KOH + HCl	11.25	240

[a] FDMH = $(CH_3)_2NN=CH_2$. [b] DMTC = $[(CH_3)_2N(NH_2)_2]Cl$.

formed in the KOH dimethyltriazanium chloride reaction, standard solutions of the hydrazone in 1 N KOH solution and in water were prepared. The pH values of these solutions were adjusted by titrating them with 5.0 N NaOH solution to the same pH as that of the reaction solutions. This titration yielded solutions with ultraviolet spectra closely resembling those of the reaction mixtures. The wavelength of maximum absorbance was consistently between 234 and 236 nm as in the case of the reaction solutions. A plot of absorbance at 234 nm vs. hydrazone concentration is shown in Figure 2. This plot was used to determine the hydrazone concentrations of the various reaction mixtures.

Hydrolysis of Dimethyltriazanium Chloride in 1 N KOH as a Function of Dimethyltriazanium Chloride Concentration. The solutions of dimethyltriazanium chloride were prepared by dissolving known amounts in 1 N KOH solution. The various products obtained by the hydrolysis were analyzed by using a Beckman DB spectrophotometer and the calibration curve in Figure 2. The results are summarized in Table IV. The only product identified was the hydrazone.

Hydrolysis of Dimethyltriazanium Chloride in Aqueous Base—Ultraviolet Analysis. The solutions of dimethyltriazanium chloride were prepared by dissolving known amounts (0.1–1.0 mg/mL) OH solutions with pH values higher than 11. Reference solu' of unsymmetrical dimethylhydrazine and the dimethylhydraz of formaldehyde were prepared in the range of 2.6×10^{-5} to 4.2×10^{-4} M. Solutions of these two substances were also prepared in a pH 1 buffer (borate, K_2CO_3, and KOH). The solutions were analyzed ultraviolet spectrophotometry (400–230 nm) using a Beckman Di
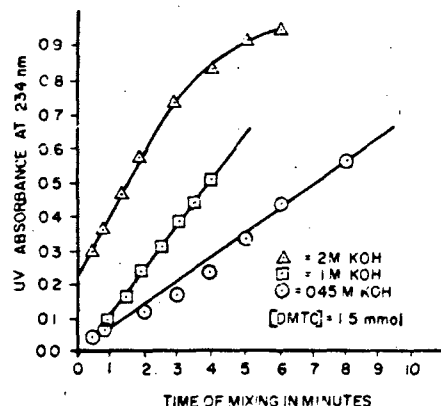

Figure 3. Hydrolysis of $[(CH_3)_2N(NH_2)_2]Cl$ (DMTC) in aqueous base.

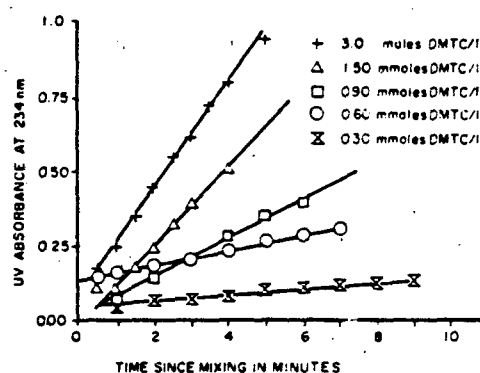**Figure 4.** Absorbance at 234 nm of $[(CH_3)_2N(NH_2)_2]Cl$ solutions of various concentrations in 1 N KOH solution vs. time after mixing.
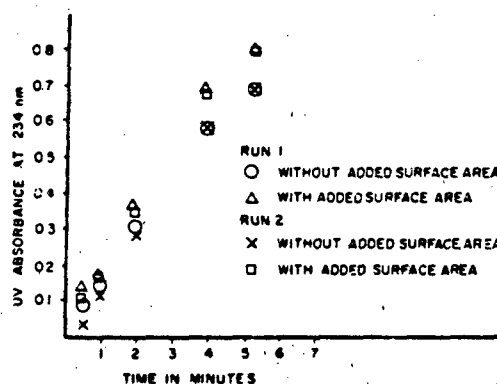

Figure 5. Effect of surface area on the hydrolysis of $[(CH_3)_2N(NH_2)_2]Cl$ in aqueous KOH solutions.

spectrophotometer. The results of the various measurements are listed in Table V.

Kinetic Studies of the Hydrolysis of Dimethyltriazanium Chloride in Aqueous Base. The rate of formation of formaldehyde dimethylhydrazone in the solutions of dimethyltriazanium chloride in potassium hydroxide was studied by monitoring the change in absorption of the solution at 234 nm. A 1-mL aliquot of solution of appropriate concentration was pipetted into an ultraviolet cell. Into this cell was injected 2.0 mL of potassium hydroxide solution of appropriate concentration. The mixing time was less than 5 s. The sample holder of the spectrophotometer was enclosed in a water jacket and the temperature was maintained at 25 °C. The changes in ultraviolet absorption with time at various potassium hydroxide concentrations and at a fixed concentration of the triazanium salt are shown in Figure 3. The final concentration of the hydrazone measured 0.5–1 h after mixing was the same for all concentrations of KOH. Similar experiments were performed with a single potassium hydroxide concentration (at 1.5 N KOH) and various initial dimethyltriazanium

Pyrolysis and Hydrolysis of Dimethyltriazanium Chloride

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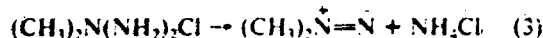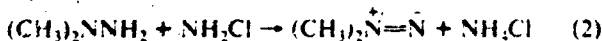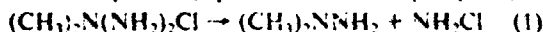chloride concentrations. These results are shown in Figure 4.

In one series of experiments half of the reaction cell was filled with broken glass to test the effect of surface area on the rate of reaction. The results obtained in these studies were identical within the limits of the experimental error with those obtained in the absence of added surface (Figure 5). The three experiments performed in 1.0 N KOH with no broken glass yielded lines with slopes of 0.165 ± 0.002 (arbitrary units) and the two experiments performed with added broken glass yielded slopes of 0.167 ± 0.01 (arbitrary units).

Hydrolysis of Dimethyltriazanium Chloride in Oxygen-Free 0.67 N KOH. The 250-mL portions of deionized water and 1.0 N KOH were purged of dissolved oxygen by passing nitrogen gas through the solutions for 16 h. The two solutions were connected in series, with the water first to saturate the nitrogen and minimize the evaporation of 1 N KOH solution. Less than 5% evaporation of the potassium hydroxide solution was observed. Several 15-mg samples of the triazanium chloride were weighed out and placed in a glovebag which was purged with nitrogen for 16 h. These samples were then dissolved in 15 mL of oxygen-free water and treated with 30 mL of oxygen-free 1 N KOH. The final concentrations of the triazanium chloride and hydroxide ions were thus 0.0030 and 0.67 M, respectively. Samples of these solutions were analyzed on the gas chromatograph 5, 10 and 60 min after mixing. All mixing was carried out in the nitrogen atmosphere of the glovebag, and all samples were taken with gastight syringes which had been previously cleaned with oxygen-free water. In all cases the only product observed was formaldehyde dimethylhydrazone.
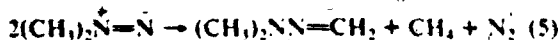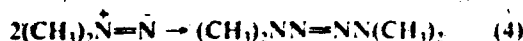
Results and Discussion

2,2-Dimethyltriazanium chloride as prepared and purified by the procedure described in the literature[10,11] contains a small amount of NH_4Cl as an impurity and melts at 134–135.5 °C. However, by use of a modified method of recrystallization, the ammonium chloride was eliminated and the melting point was decreased to 124 °C. (The presence of ammonium chloride causes the melting point of dimethyltriazanium chloride to rise.[11])

The products of the solid-state pyrolysis of the triazanium salt under vacuum with or without NaOH as analyzed by gas chromatography showed mainly the hydrazone, a small amount of tetramethyltetrazene, and trace amounts of some unidentified products. A large amount of nitrogen gas was also obtained. However, no dimethylhydrazine or chloramine was detected. From the data listed in Table III it is apparent that no simple relationship exists either between the amount of the triazanium salt pyrolyzed and the amount of the hydrazone and tetramethyltetrazene formed or between the amount of NaOH taken and the amount of the hydrazone and tetramethyltetrazene detected. On the other hand, the pyrolysis of the triazanium salt using the Pyroprobe-100 in a helium atmosphere (Tables I and II) gave dimethylhydrazine and tetramethyltetrazene in small amounts and formaldehyde dimethylhydrazone and nitrogen gas in large amounts. Two other unidentified products were also detected in small amounts. On the basis of the results of these two series of experiments, we believe that dimethyldiazine $((CH_3)_2{}^+N=N^-)$ is formed as a result of the dissociation of $(CH_3)_2N(NH_2)_2Cl$ either in two steps[8,22,23] (eq 1, 2) or in one step (eq 3). In

$$(CH_3)_2N(NH_2)_2Cl \rightarrow (CH_3)_2NNH_2 + NH_2Cl \quad (1)$$

$$(CH_3)_2NNH_2 + NH_2Cl \rightarrow (CH_3)_2\overset{+}{N}=N^- + NH_4Cl \quad (2)$$

$$(CH_3)_2N(NH_2)_2Cl \rightarrow (CH_3)_2\overset{+}{N}=N^- + NH_4Cl \quad (3)$$

either case the dimethyldiazine produced reacts further to give tetramethyltetrazene[24] and $(CH_3)_2NN=CH_2$[8,22,23] as shown by eq 4 and 5, respectively. In the pyrolysis of the triazanium

$$2(CH_3)_2\overset{+}{N}=N^- \rightarrow (CH_3)_2NN=NN(CH_3)_2 \quad (4)$$

$$2(CH_3)_2\overset{+}{N}=N^- \rightarrow (CH_3)_2NN=CH_2 + CH_4 + N_2 \quad (5)$$

chloride in a helium atmosphere all the products except NH_4Cl

and CH_4 were identified in variable amounts. The reason CH_4 was not detected is the fact that the retention times of CH_4 and N_2 are very close to each other, methane being slower by less than one-tenth of a minute. Chloramine is too reactive to be detected on the gas chromatograph.

The interesting fact to note here is that no dimethylhydrazine was detected when the pyrolysis of the triazanium salt was carried out under vacuum, whereas some was found when the pyrolysis was carried out in a helium atmosphere. One can explain this difference in terms of the experimental conditions in the two series of experiments. In the former series the $(CH_3)_2NNH_2$ and NH_2Cl (if formed) by the pyrolysis remained in the reaction zone and had a chance to react to give NH_4Cl, N_2, $(CH_3)_2NN=NN(CH_3)_2$, $(CH_3)_2NNH_2$, and CH_4 whereas, in the latter situation, the opportunity for such reaction was reduced since $(CH_3)_2NNH_2$ and NH_2Cl would be carried away from the reaction zone by the flow of helium and separated in the gas chromatography column.

Ultraviolet absorption spectrophotometry was found to be a satisfactory method for the quantitative analysis of formaldehyde dimethylhydrazone in aqueous solution. However, several problems were encountered in the use of this technique. The absorption maximum of an aqueous solution of the pure hydrazone is between 234 and 240 nm. Basic solutions have a strong absorption at 222 nm associated with the solvent. Even at 234 to 240 nm there is some background absorption by the solvent. Use of 1 N KOH as a reference solution in the double-beam spectrophotometer partially alleviated this problem but the apparent wavelength of maximum absorbance remained highly pH dependent.

The reaction mixture of dimethyltriazanium chloride and potassium hydroxide solutions exhibits a similar absorption to that of the hydrazone but at a somewhat shorter wavelength (230–235 nm). This difference is caused by a difference in pH of the solutions (Table V). It can be seen that the spectra in the two solutions have quite similar absorption maxima at the same pH. Particularly striking is the shift to 240 nm of the triazanium salt–reaction solution at pH 11.25 and the shift to the shorter wavelength (232–230 nm) of the hydrazone with the addition of more base.

On the basis of the ultraviolet measurements of the hydrolysis products of dimethyltriazanium chloride and the comparison of them with the ultraviolet absorption of various possible products of the hydrolysis, the possibility of tetramethyltetrazene as the reaction product can be ruled out. The absorption spectrum of tetramethyltetrazene is rather distinctive[18] and contains two peaks—one at 248 nm and the other at 277 nm. No such absorptions were detected in the hydrolysis products of the triazanium salt. A weak absorbance at 280 nm was observed when the solutions were allowed to stand for a long period of time. It is not clear whether this long wavelength "tail" results from some other absorption or from a trace amount of tetramethyltetrazene.
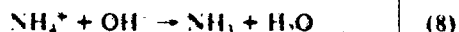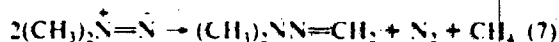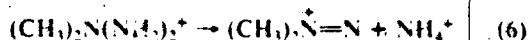
The principal product of the hydrolysis of dimethyltriazanium chloride in aqueous base is the dimethylhydrazone of formaldehyde. The ultraviolet analysis, particularly the similarity in pH dependence of the spectra of the hydrazone and the reaction products of dimethyltriazanium chloride, supports this conclusion (Table V). In addition, the gas chromatography analysis of the samples of the hydrolysis products showed a peak with retention time 5.5 min (the retention time of pure hydrazone under similar conditions is 5.5 min). This is also consistent with the formation of the hydrazone. There was initially some confusion as to the identity of the product because another suspected product, methanol, has a similar ultraviolet absorption and its retention time on the gas chromatography (5.3 min) is close to that of the hydrazone. Addition of a quantity of methanol to the

reaction mixture produced a new peak in the chromatograph whereas the addition of the hydrazone only enhanced the intensity of the peak which was already present. This also supported the identification of the reaction product as the hydrazone.
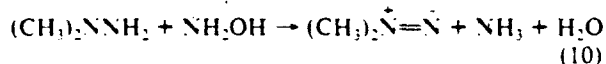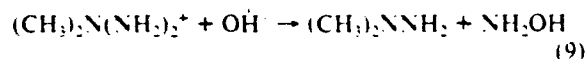
The rate of formation of the hydrazone from the triazanium salt was studied by monitoring the change in ultraviolet absorbance with time. By use of Beer's law, absorbance was taken as proportional to the concentration of the hydrazone. Therefore, the plots of absorbance vs. time are indicative of the change in concentration of the hydrazone with time. These results are shown in Figure 3. It can easily be seen that increasing the concentration of the hydroxide and holding the triazanium salt concentration at 1.5×10^{-3} M speed up the formation of the hydrazone but the results fit no simple kinetic scheme. The results of similar experiments with a constant potassium hydroxide concentration and $[(CH_3)_2N(NH_2)_2]Cl$ concentrations of 3.0×10^{-3}, 1.5×10^{-3}, 0.9×10^{-3}, 0.6×10^{-3}, and 0.3×10^{-3} M are shown in Figure 4. By use of two independent techniques,[25] these data show the rate of formation of the hyrazone to be approximately first order in $[(CH_3)_2N(NH_2)_2]Cl$ with a pseudo-first-order rate constant of $(2.8 \pm 0.5) \times 10^{-3}$ s^{-1}. The addition of extra surface does not affect the rate of reaction (Figure 6).

From the limiting absorbances of the solution usually obtained 0.5-1 h after mixing, one can obtain the final concentration of formaldehyde dimethylhydrazone in the reaction mixture (Table IV). In general the amount of the hydrazone obtained accounted for approximately 33% of the triazanium salt initially used. The rest of the salt gives products which were not detected by ultraviolet spectroscopy or by gas chromatography.

The only clearly identified product of the hydrolysis of dimethyltriazanium chloride in basic aqueous solutions obtained in these experiments was the dimethylhydrazone of formaldehyde. There is evidence that some other unidentified gaseous products were also formed. Utvary[15] has suggested that the hydrolysis of dimethyltriazanium chloride is a complex process and proposed the formation of dimethylhydrazine and dimethylamine as possible hydrolysis products. We analyzed our reaction mixtures by both ultraviolet spectroscopy and gas chromatography. Dimethylhydrazine is transparent in the ultraviolet, but there is no difficulty in identifying it by gas chromatography. Hydrolysis of the triazanium salt was performed in oxygen-free KOH solution under an oxygen-free atmosphere to avoid possible oxidation of dimethylhydrazine by oxygen;[26] yet no dimethylhydrazine was detected in the hydrolysis products. Attempts to identify dimethylamine as a salt of picric acid were also unsuccessful. In absence of any external oxidizing agent, the absence of dimethylhydrazine and dimethylamine leads to the following two conclusions: either the hydrolysis of the triazanium salt takes place as shown via

$$(CH_3)_2N(NH_3)_2^+ \rightarrow (CH_3)_2\overset{+}{N}=N + NH_4^+ \quad (6)$$

$$2(CH_3)_2\overset{+}{N}=N \rightarrow (CH_3)_2NN=CH_2 + N_2 + CH_4 \quad (7)$$

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O \quad (8)$$

or it follows a path shown by

$$(CH_3)_2N(NH_2)_2^+ + OH^- \rightarrow (CH_3)_2NNH_2 + NH_2OH \quad (9)$$

$$(CH_3)_2NNH_2 + NH_2OH \rightarrow (CH_3)_2\overset{+}{N}=N + NH_3 + H_2O \quad (10)$$

In either instance the dimethyldiazine produced would be expected to react to give[9,10,24] the hydrazone. The observed odor of NH_3 and the other gaseous products detected are consistent with the proposed mechanism.

Registry No. $[(CH_3)_2N(NH_2)_2]Cl$, 13166-44-4; $(CH_3)_2NN=CH_2$, 2035-89-4.

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Appendix IV

OXIDATION OF 1,1-DIMETHYLHYDRAZINE AND MONOMETHYLHYDRAZINE BY OXYGEN[1]

by

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Introduction

1,1-Dimethylhydrazine ($(CH_3)_2NNH_2$), a component of several rocket fuels, has been most commonly manufactured by the catalytic reduction of N-dimethylnitrosamine.[2] Since N-dimethylnitrosamine is now known to be a carcinogen[3], its use as the starting material has become much less attractive, and other processes have been sought. However, during the storage, transportation and routine handling of 1,1-dimethylhydrazine and during its use in the areas other than as a rocket fuel, 1,1-dimethyl-hydrazine may be exposed to the atmosphere and can itself possibly be oxidized to N-dimethylnitrosamine. It is important to obtain definitive data concerning such a possibility.

The oxidation of 1,1-dimethylhydrazine with air[4-8], nitrogen dioxide[9,] nitrous acid[10], hydrogen peroxide[11], bromate[12,13], halogens[12], and ozone[14] at or near room temperature has been the object of some study. However, the amount of published data is small and the identities of the oxidation products have not been clearly established. The objective of this study, therefore, was to investigate the oxidation of 1,1-dimethylhydrazine with elemental oxygen in solution under well-defined conditions to answer the basic questions: (a) Is N-dimethylnitrosamine produced by the oxidation of 1,1-dimethylhydrazine with oxygen? (b) What are the other oxidation products of this reaction? and (c) What are the kinetics of the oxidation reaction? The study of the oxidation of monomethylhydrazine is also important, mainly from the point of view of synthesis, toxicology, pollution, and combustion. Although monomethylhydrazine reacts readily with oxygen in the air, this reaction has been studied only to a limited extent. Molecular nitrogen and methane have been reported to be the major products

of this reaction[15,16]. A recent report by Saunders and Larkins[17] states
that there are seventeen products of this oxidation identified by infrared
and mass spectra. However, their report gives no details concerning the
identification of these products.

Experimental

Materials. 1,1-Dimethylhydrazine employed for this study was obtained
from the Rocky Mountain Arsenal and monomethylhydrazine was purchased from
the Aldrich Chemical Co. These hydrazines were refluxed and distilled over
solid KOH one day before use and were stored at $-4^{\circ}C$. The formaldehyde
1,1-dimethylhydrazone $((CH_3)_2NN=CH_2)$ was always present as a minor impurity
in dimethylhydrazine. Appropriate corrections were applied for this impurity
in all the calculations. 1,1,4,4-Tetramethyl-2-tetrazene[11], formaldehyde
1,1-dimethylhydrazone[18], and N-dimethylnitrosamine[19], and sym. hexahydro-
1,4-dimethyltetrazine[20] were prepared by the procedures reported in the
literature, and their purities were checked by ^1H nmr and gas chromato-
graphic analyses. The solvents used in this study were reagent grade and
were dried by refluxing and distilling them over calcium hydride, and were
stored over calcium hydride. Oxygen was supplied by AIRCO, Inc., Montvale,
New Jersey, and was used without purification except for drying with
Drierite.

Apparatus. A combination of a YSI Model - 71A and a Sargent Ther-
monitor Temperature controller was used to control the temperature of the
reaction bath within $\pm 0.05^{\circ}C$. A Brinkman IC-6 cooler was used to cool the
bath and heaters of appropriate capacity were used to heat the bath. The

reaction vessel used in this study was a 2.45 liter flask with an inlet and outlet for oxygen and a sample withdrawing port as shown in Fig. 1.

Procedure. The reaction vessel was dried at $150^{\circ}C$ for 24 hrs. The inlet of the vessel was connected to nitrogen and oxygen sources through a three-way stop cock, and the outlet vented to the hood. A magnetic stirring bar was added to the vessel, and the sample withdrawing port was closed with a rubber septum. The vessel was placed over the magnetic stirrer in the temperature controlled bath, and dry nitrogen was passed through it to expel air and moisture from the inside of the vessel. After one hour, the nitrogen flush was replaced by dry oxygen. The oxygen flush was stopped after 30 min. A freshly prepared solution of 1,1-dimethylhydrazine in the desired solvent (containing 4.00 g/l of toluene as the internal standard) was introduced into the reaction vessel. The zero-time reading of the hydrazine-toluene ratio was taken on the chromatograph, and the inlet and outlet of the reaction vessel were closed. The amount of the oxygen was calculated using the ideal gas law. Similar procedures were used when a solution of monomethylhydrazine or neat hydrazines were studied as substrates.

Analyses. A Perkin Elmer-800 gas chromatograph and a Varian Model 3700 gas chromatograph were used to detect and identify the various oxidation products of the hydrazines studied. The former instrument was equipped with a differential thermal conductivity detector and a gas chromatographic 12' x 1/8" K-20 M Carbowax 15% KOH 5% on Chrom P.A.W. 80/100 mesh size column. A variety of columns and differential thermal conductivity detectors were used with the Varian instrument. Helium was used as carrier gas in both systems. The progress of the reaction was followed by analyzing the reaction mixture by gas chromatography and comparing the gas chromatographic peak areas of the various components with that of toluene used

as the internal standard. The peak areas were computed by using a manual integrator, an electronic integrator on the recorder, and by a CDS 111 Data Analyzer supplied by Varian Associates. Identification of the various reaction products was achieved by comparing their retention times with those of the known substances, by comparing proton nmr spectra, by infrared spectra, and by mass spectrometry.

Reactions of O_2 with 1,1-Dimethylhydrazine in Diethylether. In each of a series of experiments, 250 ml. of 0.2 M solution of $(CH_3)_2NNH_2$ containing 1.0 g. toluene was reaction with 91 $\pm$ 0.5 mmole of O_2 at 20°, 25°, or 30^oC in the reaction vessel described earlier. At 20^oC, for more than a 200 hr. period, no visible change in the color of the reaction solution was observed. The major products identified by gas chromatography were $(CH_3)_2NN=CH_2$, CH_4, and N_2. In some cases a trace amount of $(CH_3)_2NN=NN(CH_3)_2$ was also observed. At 25° and 30^oC, the reaction solution changed to a light yellow color within a period of 24 hrs. In the initial stages (48 to 78 hrs) of the reactions, mainly $(CH_3)_2NN=CH_2$, CH_4, N_2 were observed as the reaction products; however, as the reaction time was increased, H_2O, $(CH_3)_2NN=NN(CH_3)_2$, and $(CH_3)_2NN=O$ also began to be observed. The rate of oxidation was measured by gas chromatographic analysis comparing the peak areas of $(CH_3)_2NNH_2$ or $(CH_3)_2NN=CH_2$ peaks with that of toluene as a function of time.

After the rate measurements of the $(CH_3)_2NNH_2$ and O_2 reaction at 25^oC in diethylether, the excess ether was evaporated in vacuum. The residual liquid was brown in color and had an irritating, disagreeable odor. This liquid was only partially soluble in H_2O, CCl_4, or dimethyl sulfoxide.

(a) <u>Proton nmr spectrum of the residual liquid</u>. The proton nmr spectrum of the portion of the residual liquid soluble in dimethyl $\underline{d}_3$-sulfoxide showed peaks corresponding to unreacted $(CH_3)_2NNH_2$, solvent $(C_2H_5)_2O$, the internal standard $C_6H_5CH_3$, and the reaction products H_2O, $(CH_3)_2NN=CH_2$, $CH_3NHN=CH_2$ and its dimer, and $(CH_3)_2NN=NN(CH_3)_2$. The proton nmr spectrum of the portion of the liquid soluble in CCl_4 showed a doublet[21] corresponding to $(CH_3)_2NNO$, in addition to those observed in dimethyl $\underline{d}_3$-sulfoxide solution, but no peak corresponding to H_2O. In addition to these peaks, there were several other peaks observed in both the solvents. The origin of some of these peaks has not yet been determined.

(b) <u>The gas chromatographic analysis of the residual liquid</u>. A gas chromatographic analysis of this liquid on a 10% Carbowax 20 M + 5% KOH column at $80°C$ on a Varian 3700 showed 22 substances with retention times between 0.60 min. to 69.70 min. (Table I). By comparing the reaction times of these substances with that of known substances, some of the substances were shown to be $(C_2H_5)_2O$, $(CH_3)_2NNH_2$, $(CH_3)_2NN=CH_2$, $(CH_3)_2NN=NN(CH_3)_2$, H_2O, $(CH_3)_2NN=NN(CH_3)_2$, $CH_3NHN=CH_2$ syn. hexahydro-1,4-dimethyltetrazine, $C_6H_5CH_3$ and $(CH_3)_2NNO$. Diethylether was the solvent and $C_6H_5CH_3$ was the internal standard used in the experiment. The carbowax column is a high polarity column for basic compounds; therefore, the substances having higher retention time are either highly polar substances or they have higher molecular weights and higher boiling points. Particularly of interest is the substance having a retention of 4.74 min., since a similar retention time is observed in the oxidation products of CH_3NHNH_2 with oxygen. The identities of the remaining substances have not yet been determined.

Table I.

Gas Chromatographic Data of the Oxidation Products

of 1,1-Dimethylhydrazine

Retention Time (Min)	G.C. % Area	Assignments
.45	.12	N_2, CH_4, NH_3
.57	54.88*	
1.30	0.07	
1.79	6.24	$(CH_3)_2NN=CH_2$
2.48	0.53	
2.82	0.13	
3.27	0.28	
4.14	3.45**	
4.61	3.07	$CH_3NHN=CH_2$ and its dimer
6.16	2.37	H_2O
6.85	4.75	$(CH_3)_2NN=NN(CH_3)_2$
9.25	4.80	
14.45	1.73	
20.74	5.78	$(CH_3)_2NN=O$
24.62	1.09	
30.59	2.30	
34.07	6.33	
39.40	1.27	
43.35	0.84	

(continued)

49.75	0.01
61.91	0.00
69.70	0.05

*Diethylether used as solvent
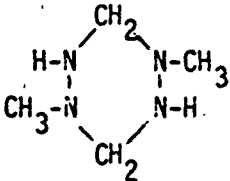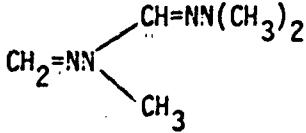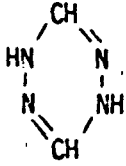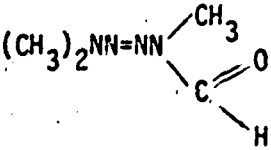
**Toluene used as internal standard

(c) <u>The mass spectral analysis of the residual liquid</u>. The gas chromatograph-mass spectral analysis of the residual liquid was done on an AEI MS-30 mass spectrometer and PYE-Unicam-104 series gas chromatograph. A 9' x ¼", 3% OV 211 column was used between 100° and 250°C (programmed for 10°/min. heating rate). The gas chromatogram of the product showed the presence of 21 substances. The mass spectrum of each of the substances was recorded. The upper m/e limit of one of the substances was 280 and there were several substances having upper m/e limits above 116. This means that there are several products having molecular weights higher than 1,1,4,4-tetramethyl-2-tetrazene (m/e=116) were formed due to the oxidation of $(CH_3)_2NNH_2$. On the basis of available evidence, the identities of some of the oxidation products are determined or postulated. These are listed in Table II.

Table II.

The Products of the Reaction of 1,1-Dimethylhydrazine with

Molecular Oxygen

Product	Basis of Identification	Mass Spectra m/e values	Remarks
N_2	GC		Confirmed
CH_4	GC		Confirmed
NH_3	GC		Confirmed

(continued)

Compound	Method	MS fragments	Status
H_2O	GC, NMR		Confirmed
$(CH_3)_2NN=CH_2$	GC, NMR		Confirmed
$(CH_3)_2NNO$	GC, NMR, MS	74, 59, 58, 44, 43, 42, 29	Confirmed
$(CH_3NHN=CH_2$	GC, NMR		Confirmed

(first cyclic structure)	GC	116, 115, 114, 100, 73, 72, 71, 70, 59, 58, 57, 44, 43, 29	Confirmed
$(CH_3)_2NN=NN(CH_3)_2$	GC, NMR, MS	116, 72, 58, 44, et al.	Confirmed
(branched structure with $CH=NN(CH_3)_2$, $CH_2=NN$, CH_3)	MS	114, 84, 71, 70, 58, 44, 42	Postulated
$(CH_3)_2NNH(CH_3)$	MS	74, 73, 70, 59, 58, 44, 30, 29	Postulated
(six-membered HN/N ring structure)	MS	83, 56, 44, 42, 30, 29	Postulated
$(CH_3)_2NN=NN$ (with CH_3, $C=O$, H)	MS	130, 129, 86, 85, 84, 83, 72, 70, 59, 58, 57, 56, 46, 45, 44, 43, 42	Postulated

Reaction of O_2 with $(CH_3)_2NNH_2$ in Cyclohexane Solutions. In each of another series of experiments using cyclohexane as the solvent, 250 ml. of 0.2 M $(CH_3)_2NNH_2$ solution containing 1.0 g. of toluene was reacted with 91 ± 0.5 mmole of O_2 at 20°, 25° or 30°C. The nature of the products identi-

fied at 20° and at 25^5 and $30^\circ C$ was similar to those observed when the reaction was carried out in diethylether. The change of solvent likewise had little effect on the rate at which $(CH_3)_2NNH_2$ was oxidized. The development of yellow color was observed only when the reaction was carried out at 25° and $30^\circ C$.

Reaction of $(CH_3)_2NNH_2$ with O_2 in the Absence of a Solvent. The reaction between $(CH_3)_2NNH_2$ and O_2 in the absence of a solvent was carried out by allowing 3.0 g. of $(CH_3)_2NNH_2$ to react with 100 ± 0.5 mmole of dry oxygen at $25^\circ C$. The results are summarized in Table III.

Table III

Time in min.	Constituents of the Vapor Phase
0	$(CH_3)_2NNH_2$
85	N_2, CH_4, $(CH_3)_2NNH_2$, $(CH_3)_2NN=CH_2$
285	N_2, CH_4, $(CH_3)_2NNH_2$, $(CH_3)_2NN=CH_2$
1410	N_2, CH_4, $(CH_3)_2NNH_2$, $(CH_3)_2NN=CH_2$

No 1,1-dimethylnitrosamine was detected in the gas phase analysis. The residue which was a brown liquid was partly soluble in dimethyl sulfoxide and partly in CCl_4. The proton nmr spectrum (Fig. 2) of the residue soluble in CCl_4 contained peaks characteristic of the spectrum reported[21] for $(CH_3)_2NN=O$, whereas, the portion soluble in dimethyl sulfoxide showed nmr peaks corresponding to unreacted $(CH_3)_2NNH_2$ and $(CH_3)_2NN=NN(CH_3)_2$, $(CH_3)_2NN=CH_2$ and a small amount of H_2O. The gas chromatogram of the residue in ether is shown in Fig. 3. The presence of H_2O was further confirmed by gas chromatographic analysis of the extract of the residue with methanol.

Reaction of $(CH_3)_2NNH_2$ with a Small Amount of Oxygen in a Nitrogen
Atmosphere. The reaction vessel was filled with dry nitrogen and to it
250 ml. of 0.2 M $(CH_3)_2NNH_2$ solution containing 1.0 ml. of toluene was
added. Through the rubber septum cap 25 ml. (1.0 mmole) of dry oxygen
was injected into the flask and the inlet and the outlet of the flask
were closed. The flask was kept at 25°C. The results are summarized in
Table IX.

Table IX

Reaction Time (minutes)	0	220	310	350	4960
$(CH_3)_2NNH_2/(CH_3)_2NN=CH_2$	19	6	6	6	6

Apparently the amount of $(CH_3)_2NN=CH_2$ formed did not show an increase
after 220 min. of the reaction time. Similar results were obtained when
the solvent was changed to cyclohexane. Addition of 1 ml. water and keep-
ing the amounts of the other components the same at 25°C did not show any
different results than those observed without water.

Reaction of Monomethylhydrazine with Oxygen. The reaction of mono-
methylhydrazine with oxygen was carried out using the vessel (Fig. 1) and
the procedure described earlier. After flushing and filling the vessel
with dry oxygen, 4.0 g. (86 mmole) of monomethylhydrazine was introduced
into the flask through the septum cap by means of a hypodermic syringe,
nd the inlet and the outlet of the flask were closed. The liquid was
slowly stirred by a magnetic stirrer. An exothermic reaction started al-
most immediately. The flask was kept cool by immersing it in a water bath
at 25°C. The color of the liquid changed gradually to yellow, becoming
wine red after two hours. After standing overnight, the solution assumed

a yellow color again. The oxidation products were examined at this stage and again after three weeks by withdrawing liquid as well as gaseous samples through the rubber septum cap.

Gas chromatographic analysis of the gaseous mixture using a molecular sieve column showed the presence of oxygen, nitrogen, and methane.

Gas chromatographic analysis of the liquid reaction product after 24 hrs. showed (Fig. 4) the presence of ten components. The four major components, constituting about 92% of the total, were methanol, monomethylhydrazine, sym. hexahydro-1,4-dimethyltetrazine, and water (Table $\overline{\Sigma}$).

Table $\overline{\Sigma}$

Gas Chromatographic Data of the Oxidation Products of MMH
Liquid Sample

After 24 hrs.				After 3 weeks	
Retention time (min.)	% Area	Assignment		Retention time (min.)	% Area
0.49	.74			.51	.91
0.65	.91			.74	2.96
0.78	3.13			1.32	.26
1.34	0.50			1.51	.25
1.64	1.19			1.60	.21
1.86	12.74	$\longleftarrow CH_3OH \longrightarrow$		1.86	19.47
2.60	1.49			3.33	.03
3.54	23.73	$\longleftarrow CH_3NHNH_2 \longrightarrow$		3.72	.08
4.75	21.86	$\longleftarrow (CH_3NHN=CH_2)_2 \longrightarrow$		4.73	15.28
5.92	33.72	$\longleftarrow H_2O \longrightarrow$		6.17	60.00
				20.62	.55

(continued)

Gas Sample

<u>After 8 hrs.*</u>

1.41	24.45	$\longleftarrow O_2 \longrightarrow$	1.45	38.69
2.21	51.25	$\longleftarrow N_2 \longrightarrow$	2.29	48.74
4.15	24.30	$\longleftarrow CH_4 \longrightarrow$	4.23	12.57

*   Separate experiment

The gas chromatographic analysis of the reaction products analyzed after three weeks showed no monomethylhydrazine; however, the major oxidation products were water, methanol, and sym. hexahydro-1,4-dimethyltetrazine constituting approximately 95% of the products.

The proton nmr also showed the signals corresponding to these three products. The spectrum at higher amplification was very complicated, indicating the presence of several other minor products.

<u>Results and Discussion</u>

<u>Kinetics of the $(CH_3)_2NNH_2$-O_2 Reaction</u>. The rate of the reaction of 1,1-dimethylhydrazine with oxygen in this study can be expressed by the equation

$$\text{Rate} = -\frac{d[(CH_3)_2NNH_2]}{dt} = -\frac{d(O_2)}{dt} = k[(CH_3)_2NNH_2]^m[O_2]^n \tag{1}$$

If $\underline{a}$ is the initial molar concentration of $(CH_3)_2NNH_2$ and $\underline{a} - \underline{x}$ is its concentration at any given reaction time $\underline{t}$ in the solvent medium, then

$$-\frac{d[(CH_3)_2NNH_2]}{dt} = \underline{k}(\underline{a} - \underline{x})^m[O_2]^n \tag{2}$$

Concentrations were determined by gas chromatography using toluene as an internal standard since toluene does not enter into the oxidation reaction.

The value of $\underline{a} - \underline{x}$ can then be determined by comparing the peak areas of $(CH_3)_2NNH_2$ and of toluene on the gas chromatograph. The initial concentration of O_2 gas in the reaction system was calculated by u.. of the gas law expression, but its concentration at other times was not determined. The total order of the reaction, however, was determined by Power curves[22] in which $(\underline{a} - \underline{x}$ was plotted against ln $\underline{t}$. These plots (Fig. 5) revealed that the total order of the $(CH_3)_2NNH_2-O_2$ reaction is equal to one. Urry et al[6], studying the reaction of O_2 (air) with $(CH_3)_2NNH_2$ in the gas phase, suggested that the reaction under those circumstances is zero order with respect to O_2 and first order with respect to $(CH_3)_2NNH_2$. If it is assumed that these same orders obtain for the reaction in solution, then equation (2) may be written

$$- \frac{d[(CH_3)_2NNH_2]}{d\underline{t}} = \underline{k}'(\underline{a} - \underline{x}) \tag{3}$$

where $\underline{k}'$ is the first order rate constant, a plot of ln $(\underline{a} - \underline{x})$ vs. $\underline{t}$ should yield a straight line. Such plots based on our data are shown for various temperatures and initial concentrations do indeed give straight lines as the plots for the reaction at $30^\circ C$ in diethylether and in cyclohexane shown in Fig. 6 exemplify. The first order rate constants at 20°, 25°, and $30^\circ C$ in diethylether and in cyclohexane were calculated from the equation

$$\underline{k}' = - \frac{\ln (\underline{a} - \underline{x})}{\underline{t}} \tag{4}$$

These values are listed in Table VI. Using an Arrhenius plot (ln $\underline{k}'$ vs. $\frac{1}{T}$), the activation energies for the reaction in ether and in cyclohexane were found to be the same within experimental error, viz. 130 k-J mole^{-1}.
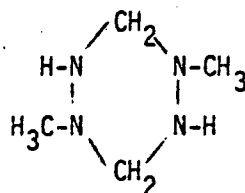
Table VI.

Specific Rate Constants of 1,1-Dimethylhydrazine Oxygen Reaction

$(CH_3)_2NNH_2$	Solvent	O_2	Temperature	$\underline{k}' \times 10^6$ sec^{-1}
250 ml. 0.20 M	Diethylether	91. $\overset{+}{-}$ 0.5 mmole	30°C	7.0
			25°C	3.8
			20°C	2.0
250 ml. 0.20 M	Cyclohexane	91. $\overset{+}{-}$ 0.5 mmole	30°C	6.4
			25°C	2.2
			20°C	2.0

Products of the Reaction $(CH_3)_2NNH_2$ and O_2. Mechanistic Considera-
Considerations. The reaction products of the oxidation of 1,1-dimethyl-
hydrazine with elemental oxygen obtained in this study number more than
twenty. In the following discussion, "percent of total" figures are based
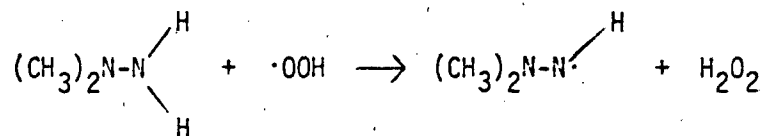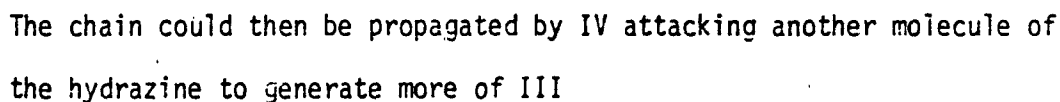on area measurements of peaks on gas chromatographs.

The major gaseous products of the reaction are N_2, CH_4, and NH_3. The
major liquid products in the reaction mixture are the dimethylhydrazone of
formaldehyde, $(CH_3)_2NN=CH_2$, 1,4-tetramethyltetrazene, $(CH_3)_2NN=NN(CH_3)_2$,
dimethylnitrosamine $(CH_3)_2NNO$, the monomethylhydrazone of formaldehyde,
$CH_3NHN=CH_2$ and its dimer, sym. hexahydro-1,4-dimethyltetrazine

$$
\begin{array}{ccc}
 & \overset{\displaystyle CH_2}{\diagup \quad \diagdown} & \\
H-N & & N-CH_3 \\
| & & | \\
H_3C-N & & N-H \\
 & \diagdown \quad \diagup & \\
 & CH_2 &
\end{array}
$$
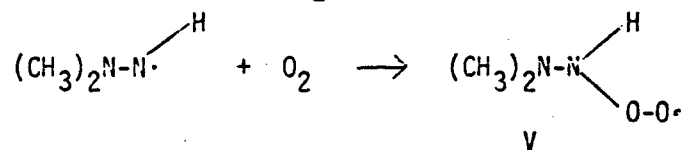
as shown in Table 1. Some of the additional products formed in lesser
quantity are discussed below.

As shown above, the reaction of $(CH_3)_2NNH_2$ with elemental oxygen in
diethylether and in cyclohexane is first order in the hydrazine and probably
zero order with respect to O_2. Similar kinetics have been observed for the
oxidation of phenylhydrazones[23] and for 1,1-dimethylhydrazine in the gas
phase[6].
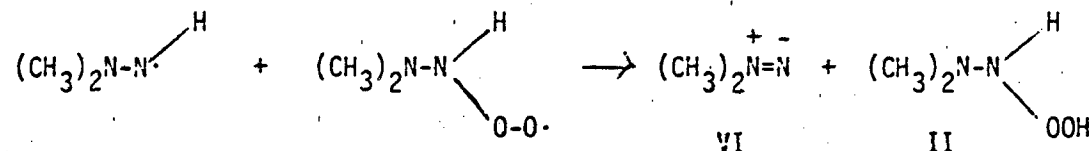
The first step in the reaction of O_2 with $(CH_3)_2NNH_2$ is probably the
formation of dimethyldiazene $((CH_3)_2\overset{+}{N}=\overset{-}{N}$. It has been suggested that the
initial step in this formation is the formation of the hydroperoxide of
the hydrazine by oxygen molecule insertion[6,7] between the N and H atoms
of the N-H bond followed by breakdown into radicals

$(CH_3)_2N-N\begin{smallmatrix}H\\\\H\end{smallmatrix}$ + O_2 $\longrightarrow$ $(CH_3)_2N-N\begin{smallmatrix}H\\\\O-OH\end{smallmatrix}$

I $\qquad\qquad\qquad$ II

$(CH_3)_2N-N\cdot^H$ + $\cdot OOH$

III $\qquad\qquad$ IV

The chain could then be propagated by IV attacking another molecule of
the hydrazine to generate more of III

$(CH_3)_2N-N\begin{smallmatrix}H\\\\H\end{smallmatrix}$ + $\cdot OOH$ $\longrightarrow$ $(CH_3)_2N-N\cdot^H$ + H_2O_2

III can also react with O_2 to form V

$(CH_3)_2N-N\cdot^H$ + O_2 $\longrightarrow$ $(CH_3)_2N-N\begin{smallmatrix}H\\\\O-O\cdot\end{smallmatrix}$

V

V can then react with more of III to form the diazene and more II

$(CH_3)_2N-N\cdot^H$ + $(CH_3)_2N-N\begin{smallmatrix}H\\\\O-O\cdot\end{smallmatrix}$ $\longrightarrow$ $(CH_3)_2\overset{+}{N}=\overset{-}{N}$ + $(CH_3)_2N-N\begin{smallmatrix}H\\\\OOH\end{smallmatrix}$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ VI $\qquad\qquad$ II

Urry et al[6] have suggested that HO· and $(CH_3)_2N-N\begin{smallmatrix}H\\\\O\end{smallmatrix}$
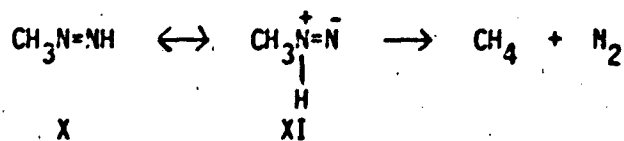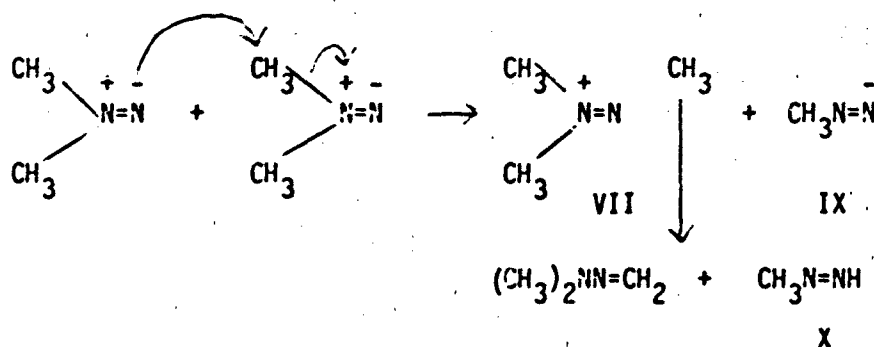
are also formed by the decomposition of II.

An alternate route for the formation of the diazene (VI from II) would
be by the following heterolytic process:

$(CH_3)_2N-N\begin{smallmatrix}H\\\\O-OH\end{smallmatrix}$ $\rightleftharpoons$ $(CH_3)_2\overset{+}{N}=N-H$ + OOH^-

II $\qquad\qquad\qquad\qquad\qquad$ VII

$$(CH_3)_2\overset{+}{N}=N-H + OOH^- \longrightarrow (CH_3)_2\overset{+}{N}=\overset{-}{N} + H_2O_2$$

VI
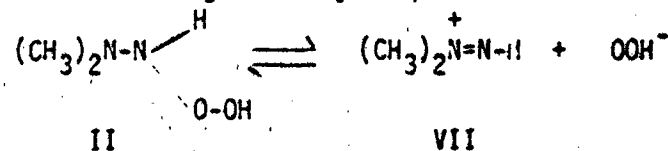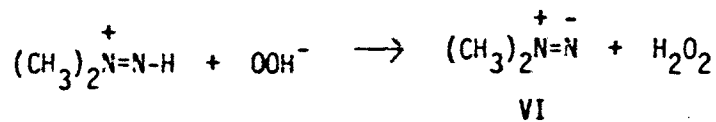
However, the values of the rate constant for this reaction were the same in diethylether and in cyclohexane. This fact would not support the postulation of an ionic mechanism, since the greater polarity of the ether should favor an ionic mechanism. However, the difference in the polarities of diethylether and cyclohexane is not great enough to make this inference conclusive.

If we assume the formation of 1,1-dimethyldiazene (VI) as the first step in the oxidation, the formation of various observed and inferred products can be explained. The formation of $(CH_3)_2NN=CH_2$ can be explained as previously reported by Sisler et al[1b]:

$$CH_3N=NH \longleftrightarrow CH_3\overset{+}{\underset{|}{N}}=\overset{-}{N} \longrightarrow CH_4 + N_2$$

$$\qquad\qquad\qquad H$$

$$\quad X \qquad\qquad\quad XI$$
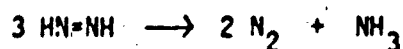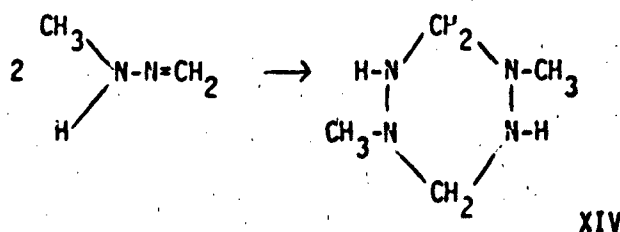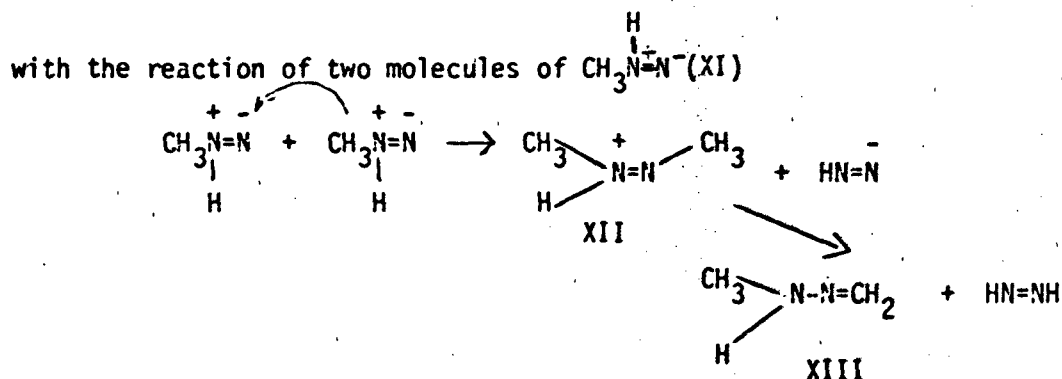
The kinetics of the formation of $(CH_3)_2NN=CH_2$ appears to follow a combination of two reactions, each second order, in $(CH_3)_2NN=CH_2$ as indicated in the plots of $\dfrac{1}{((CH_3)_2NN=CH_2)}$ vs. $\underline{t}$ (Fig. 7), and have no direct relationship with the consumption of $(CH_3)_2NNH_2$ (Fig. 6). The fact that

the rate of formation of $(CH_3)_2NN=CH_2$ is faster in the initial stages and sharply decreases after about 10 hours may be the result of the consumption of $(CH_3)_2NN=CH_2$ by secondary reactions.

The formation of tetramethyltetrazene $((CH_3)_2NN=NN(CH_3)_2)$ could readily occur through the dimerization of dimethyldiazene (VI)

$$2(CH_3)_2\overset{+}{N}=\overset{-}{N} \longrightarrow (CH_3)_2NN=NN(CH_3)_2$$
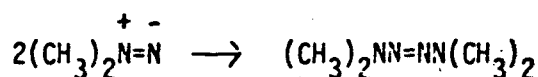
A reasonable pathway for the formation of the monomethylhydrazone of formaldehyde and its dimer, sym. hexahydro-1,4-dimethyltetrazine would begin with the reaction of two molecules of $CH_3\overset{H}{\underset{|}{\overset{+}{N}}}=\overset{-}{N}$ (XI)

$$3 \ HN=NH \longrightarrow 2 \ N_2 + NH_3$$

Both XIII and XIV are known compounds[20,24,25]. The presence of XIII in the reaction product is confirmed by the presence of a typical quartet in the proton nmr spectrum at 6.3 δ. The dimer is confirmed by the appropriate peaks in the mass spectrum. The retention times of XIII and XIV (in benzene solution) in the gas chromatographic analysis are the same.

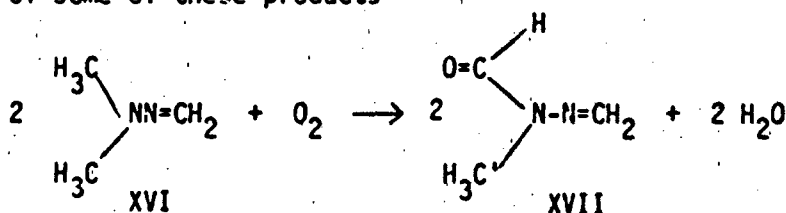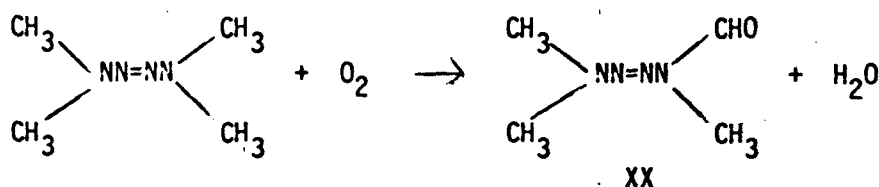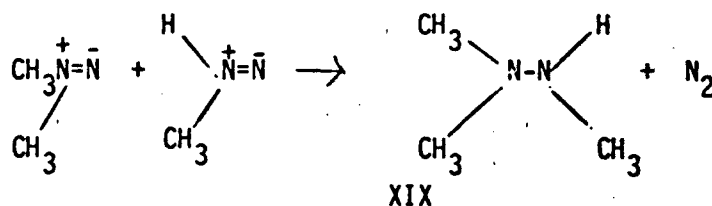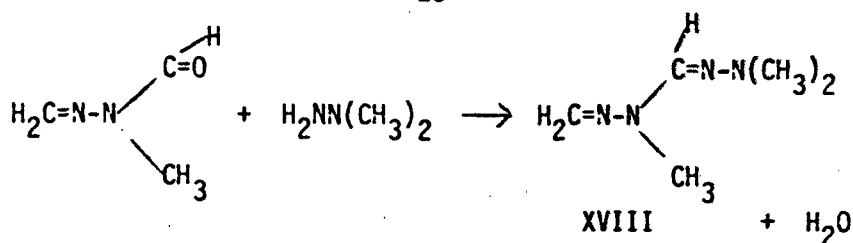Other products confirmed by proton nmr and mass spectra, and by gas chromatographic analysis include 1,1-dimethylnitrosamine ($(CH_3)_2NNO$) and water. The formation of the nitrosamine and water can occur through the decomposition of II which Urry[6] has indicated might be base catalyzed.

$$(CH_3)_2NN\overset{H}{\diagdown}\quad +\ B: \longrightarrow\ (CH_3)_2N\bar{N}\quad +\ B:H^+$$
$$\quad\quad\quad\quad OOH$$
$$II\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad OOH$$
$$XV\ \downarrow$$
$$(CH_3)_2NN=O$$
$$+$$
$$OH^-\ \xrightarrow{B:H^+}\ B:\ +\ H_2O$$
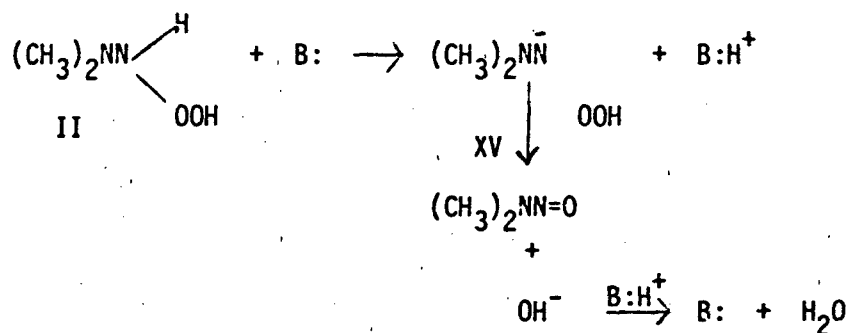
Though Urry[6] and Loper[7] have discussed the possibility of the formation of the nitrosamine in the gas phase reaction of $(CH_3)_2NNH_2$ and O_2, no quantitative data concerning the extent of its formation were given. In our studies in the liquid phase, the amount of the nitrosamine ranges between 1.5% and 13.9% of the reaction product as measured by gas chromatography.

The identities of the remaining four products listed in Table 1 are postulated on the basis of gas chromatographic and mass spectral analysis. Such reactions as the following may be postulated to account for the formation of some of these products

$$2\ \overset{H_3C}{\underset{H_3C}{\diagdown}}NN=CH_2\ +\ O_2\ \longrightarrow\ 2\ \overset{O=C\diagup^H}{\underset{H_3C}{\diagdown}}N-N=CH_2\ +\ 2\ H_2O$$
$$XVI\quad\quad\quad\quad\quad\quad\quad XVII$$

$$H_2C=N-N\begin{smallmatrix}C=O\\ \\CH_3\end{smallmatrix} + H_2NN(CH_3)_2 \longrightarrow H_2C=N-N\begin{smallmatrix}C=N-N(CH_3)_2\\ \\CH_3\end{smallmatrix}$$

XVIII   + H_2O

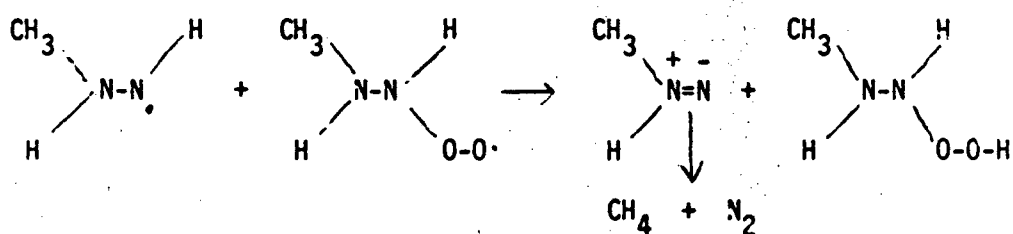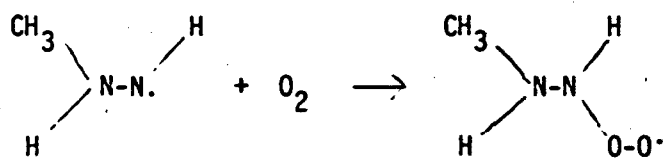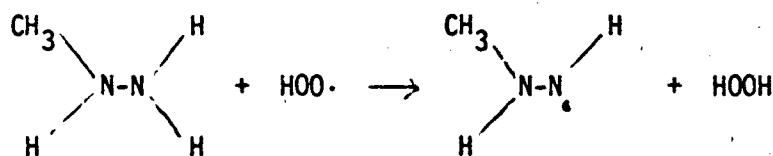$$CH_3\overset{+}{N}=\bar{N} + \overset{H}{\underset{CH_3}{\diagdown}}\overset{+}{N}=\bar{N} \longrightarrow \overset{CH_3}{\underset{CH_3}{\diagup}}N-N\overset{H}{\underset{CH_3}{\diagdown}} + N_2$$

XIX

$$\overset{CH_3}{\underset{CH_3}{\diagup}}NN=NN\overset{CH_3}{\underset{CH_3}{\diagdown}} + O_2 \longrightarrow \overset{CH_3}{\underset{CH_3}{\diagup}}NN=NN\overset{CHO}{\underset{CH_3}{\diagdown}} + H_2O$$

XX

Formation of XX has been reported from the oxidation of $(CH_3)_2NN=NN(CH_3)_2$ by chloramine[26].

$$2\ \overset{CH_3}{\underset{H}{\diagdown}}\overset{+}{N}=\overset{-}{N} \overset{O_2}{\longrightarrow}\ \text{XXI ring} + 2\ H_2O$$

XXI
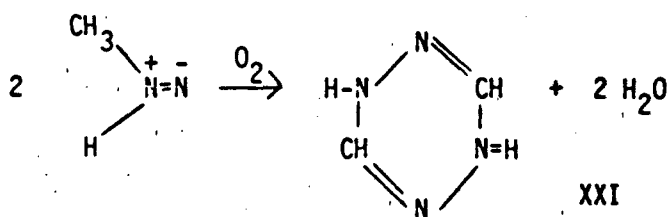
The presence of XVIII-XXI can be inferred from the various fragments observed in the gas chromatograph mass spectral analysis of the reaction mixture.

Mechanism for the $CH_3NHNH_2-O_2$ Reaction. The major products of the oxidation of monomethylhydrazine by gaseous oxygen have been shown in this study to be methane, water, nitrogen, methanol, and sym. hexahydro-1,4-dimethyltetrazine. It is reasonable to postulate the initial formation of the diradical $CH_3\overset{+}{N}H=\overset{-}{N}$ through a pathway such as the following:

$$CH_3\text{-}N\text{-}N(H)(H) + O_2 \longrightarrow CH_3\text{-}N\text{-}N(H)(O\text{-}O\text{-}H)$$

$$\longrightarrow CH_3\text{-}N\text{-}N\cdot(H) + HOO\cdot$$

$$CH_3\text{-}N\text{-}N(H)(H) + HOO\cdot \longrightarrow CH_3\text{-}N\text{-}N\cdot(H) + HOOH$$

$$CH_3\text{-}N\text{-}N\cdot(H) + O_2 \longrightarrow CH_3\text{-}N\text{-}N(H)(O\text{-}O\cdot)$$

$$CH_3\text{-}N\text{-}N\cdot(H) + CH_3\text{-}N\text{-}N(H)(O\text{-}O\cdot) \longrightarrow CH_3\text{-}N\overset{+}{=}\overset{-}{N}(H) + CH_3\text{-}N\text{-}N(H)(O\text{-}O\text{-}H)$$

$$\downarrow$$

$$CH_4 + N_2$$
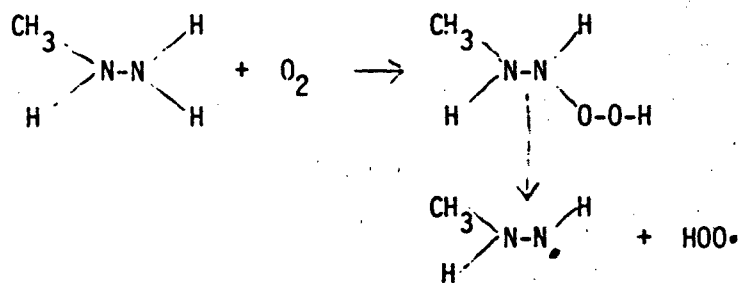
The $CH_3\overset{+}{N}H\overset{-}{=}N$ intermediate may be expected to react in a manner analogous to that proposed for $(CH_3)_2\overset{+}{N}\overset{-}{=}N$ to give the methylhydrazone of formaldehyde which then dimerizes to sym. hexahydro-1,4-dimethyltetrazine[20,25].

$$CH_3\text{-}N\overset{+}{=}\overset{-}{N}(H) + CH_3\text{-}N\overset{+}{=}\overset{-}{N}(H) \longrightarrow CH_3\text{-}N(H)\text{-}N\text{=}CH_2 + NH\text{=}NH$$

$$\downarrow$$

sym. hexahydro-1,4-dimethyltetrazine ring:

$$H\text{-}N,\ N\text{-}CH_3,\ H_3C\text{-}N,\ N\text{-}H,\ CH_2,\ CH_2$$

$$3HN\text{=}NH \longrightarrow 2N_2 + 2NH_3$$
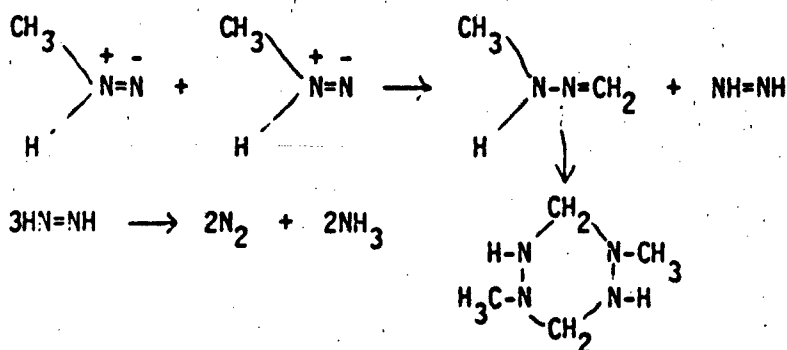
An alternate pathway would involve the direct interaction of O_2 with the $CH_3\overset{+}{N}H=\bar{N}$ intermediate either at the methyl hydrogens to give formaldehyde or at the C-N bond resulting in the formation of methanol. Water and N_2 would also be formed in each instance. The formaldehyde formed would then react with monomethylhydrazine to give the monomethylhydrazone of formaldehyde, which would dimerize as shown above.

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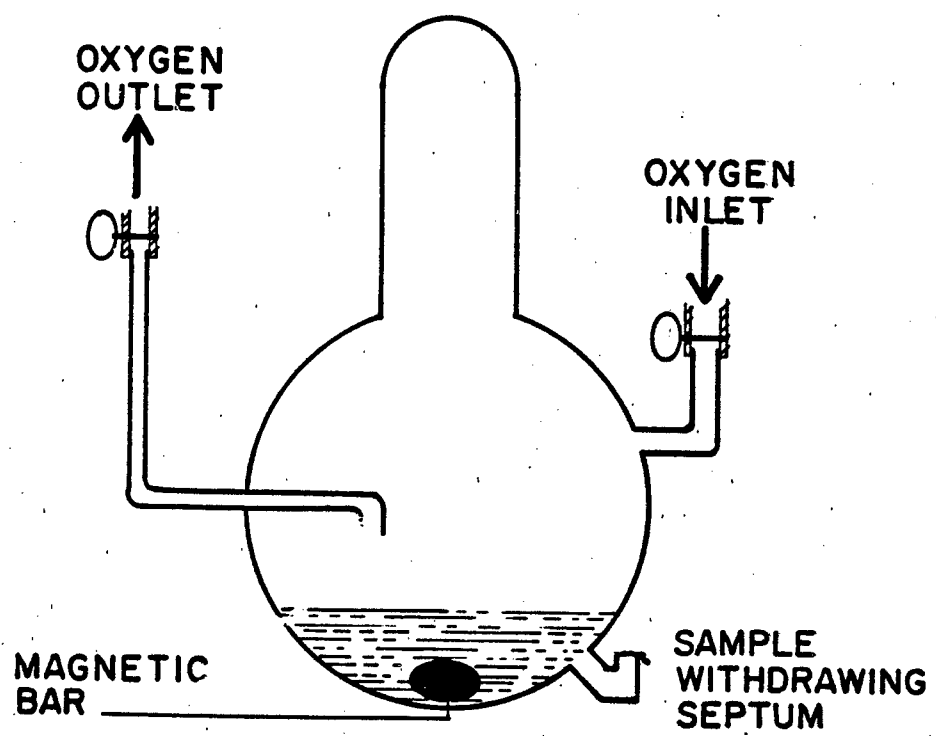
Figure 1. Reaction Vessel for the Oxidation Studies.

OXYGEN OUTLET

OXYGEN INLET

MAGNETIC BAR

SAMPLE WITHDRAWING SEPTUM

Figure 2. Proton NMR Spectrum of the Oxidation Products of
1,1-Dimethylhydrazine Showing N-Dimethylnitrosamine

δppm

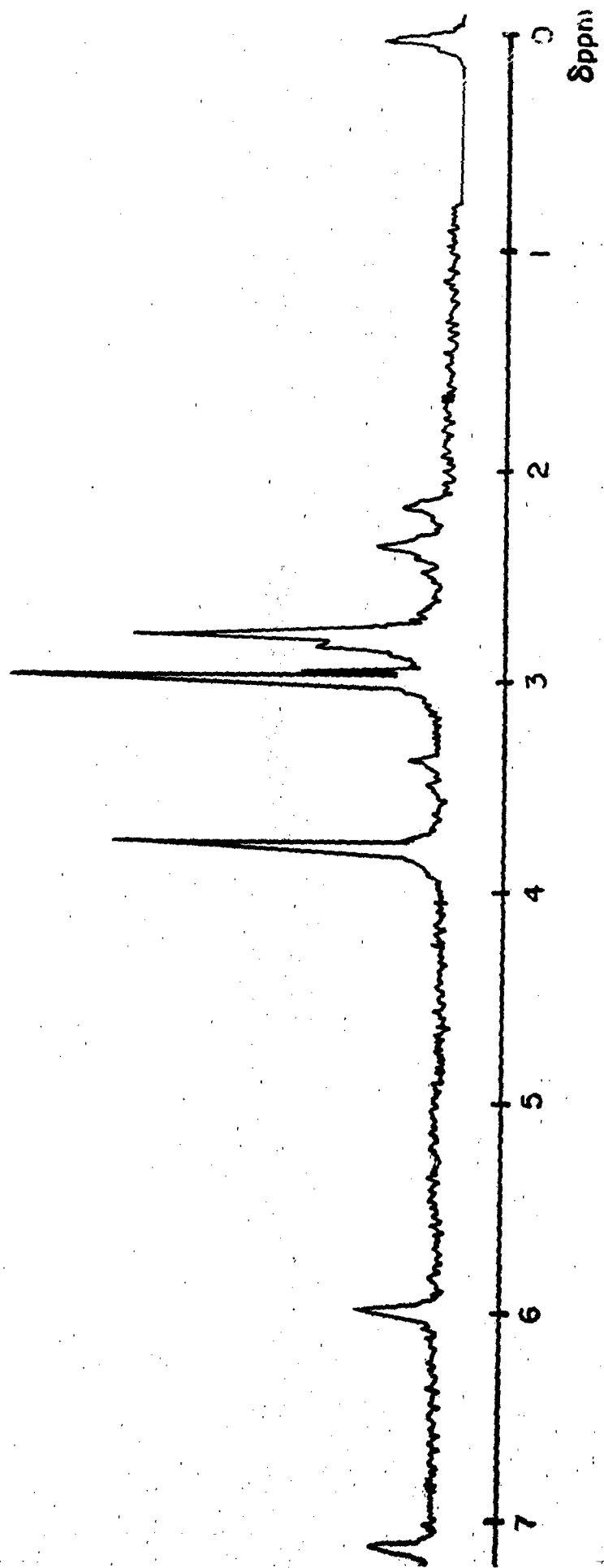Figure 3. Gas Chromatogram of the Oxidation Products of
1,1-Dimethylhydrazine in Ether

RETENTION TIME (min)

.61 .78 1.95 2.61 3.84 4.76 5.81 6.49 7.10 9.44 12.54 15.55 17.16 20.46 30 66 39 30
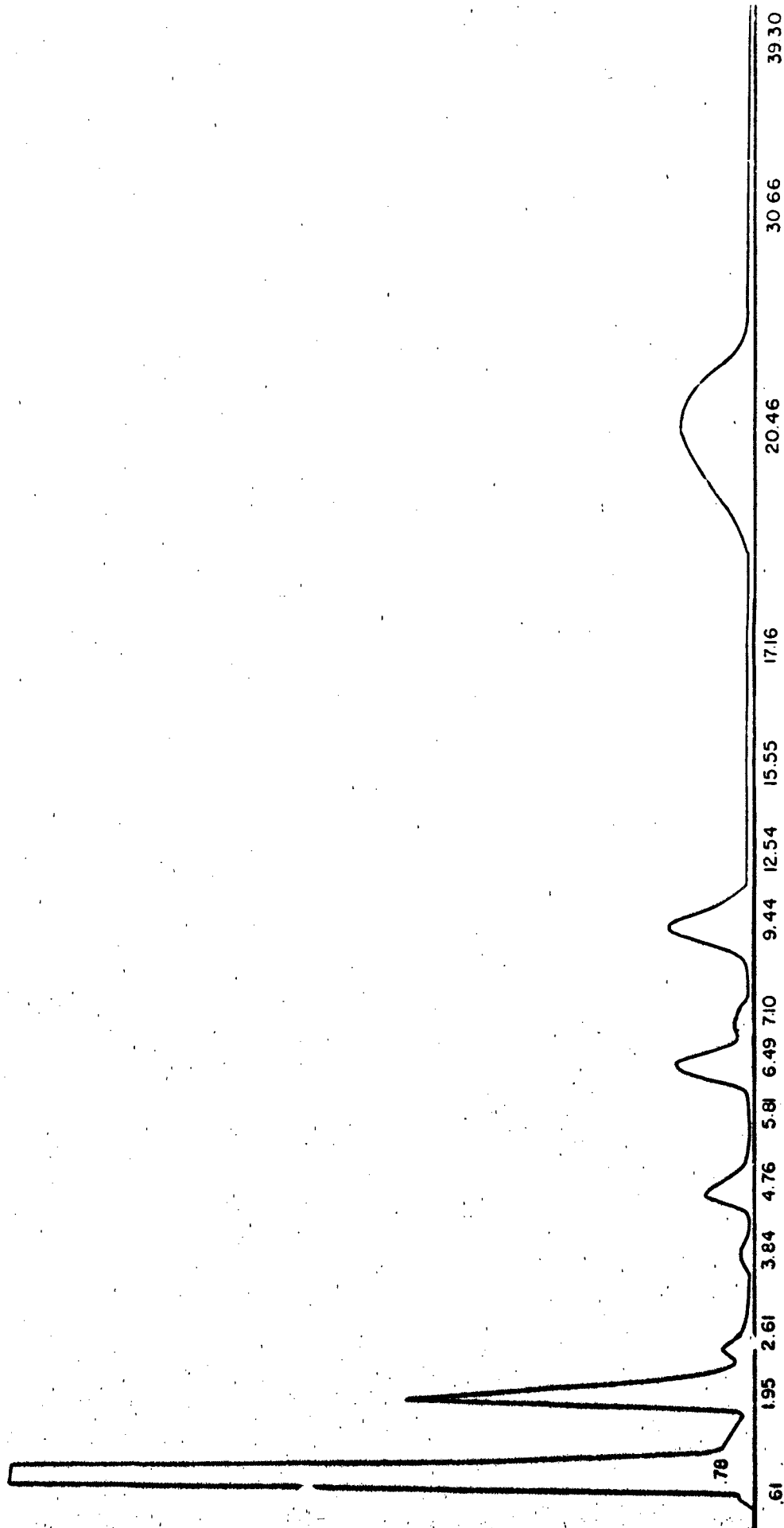
Figure 4. Gas Chromatogram of the Oxidation Products of Monomethylhydrazine

RETENTION TIME (min)

0   0.78   1.86   3.54   4.75   5.92
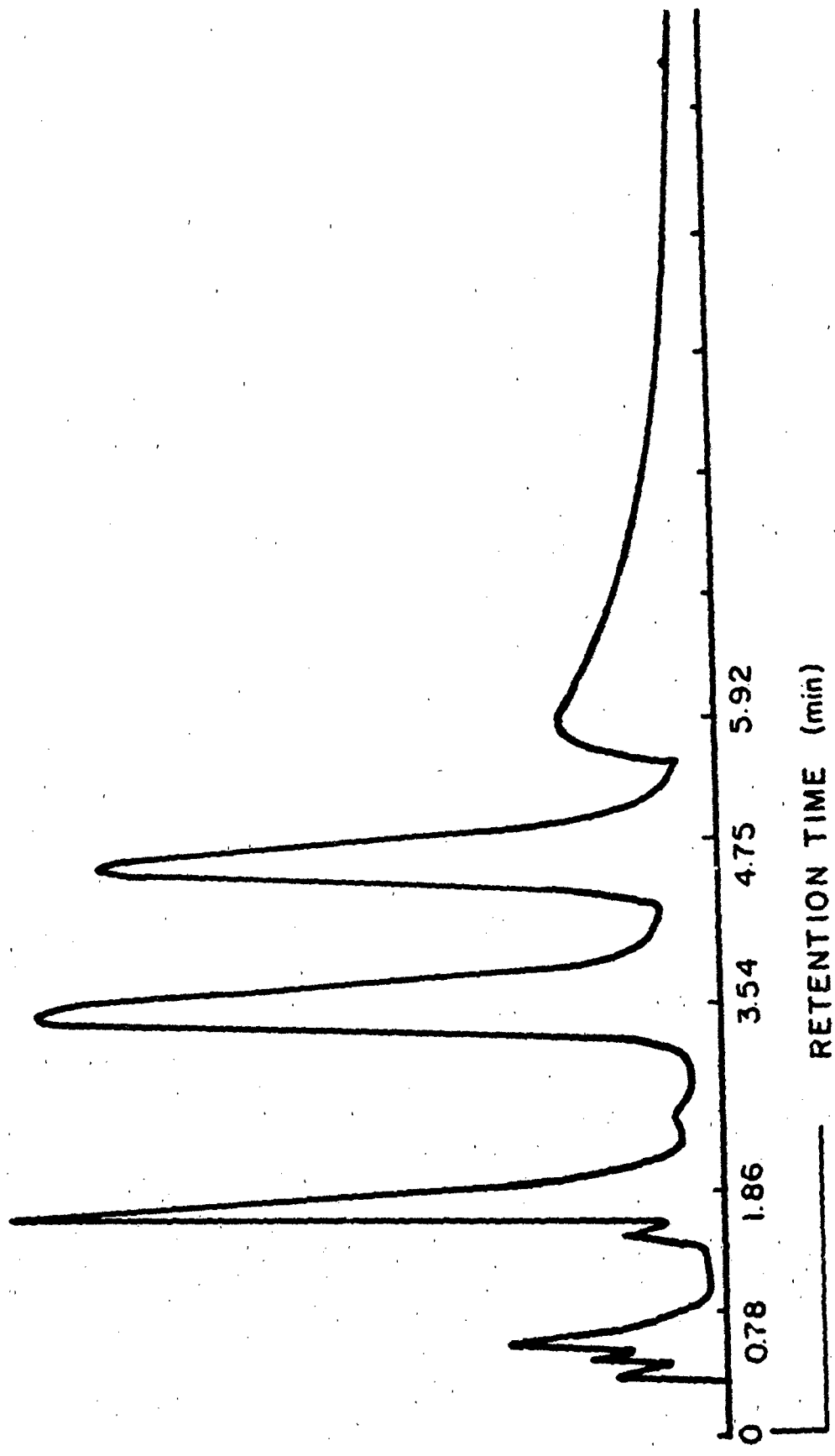
Figure 5. Powell Curves, (a - x) vs. ln(time) for the Oxidation of
1,1-Dimethylhydrazine

Fraction Remaining vs. ln t

Plot according to R. E. Powell

α Fraction remaining
Temp. 30°C.
Solvent Diethyl Ether
UDMH 0.2M in 250ml
Oxygen 91 ±0.5 mmol.

ln t
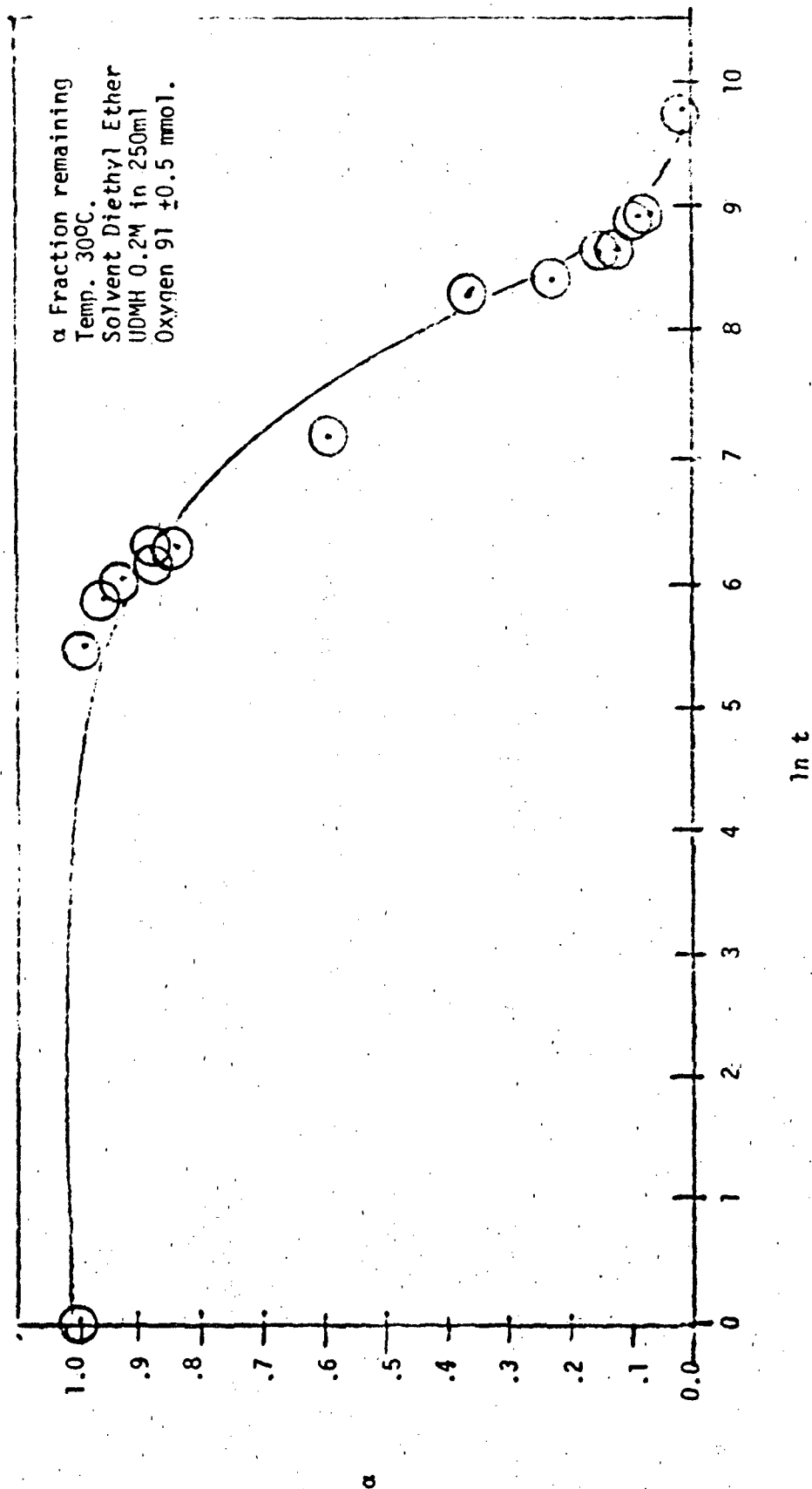
Figure 6. $\ln((CH_3)_2NNH_2)$ vs. Time Plots for $(CH_3)_2NNH_2$ Oxidation at 30° C. in Diethylether (C) and in Cyclohexane (△).
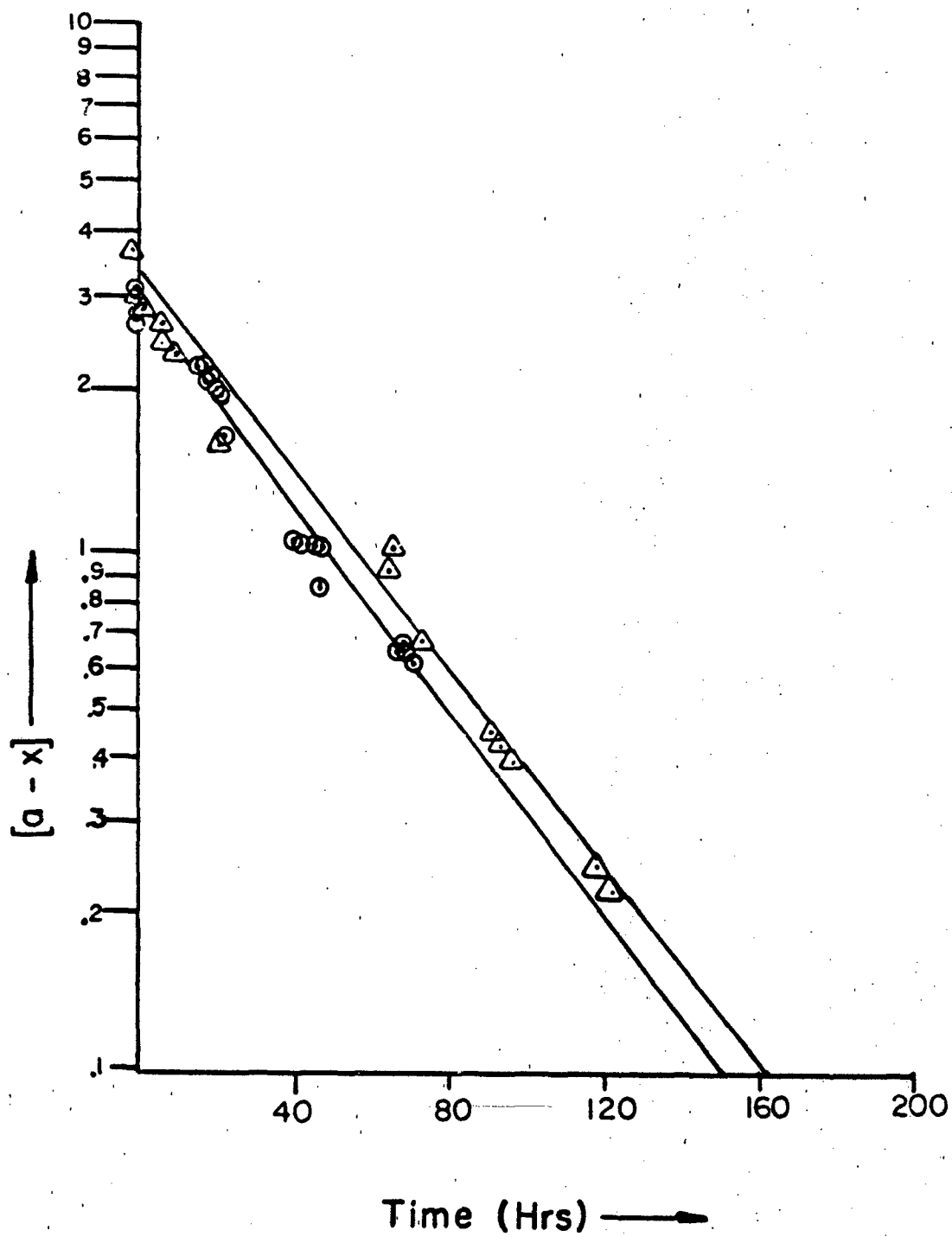
Figure 7. Plot Showing $((CH_3)_2NN=CH_2)^{-1}$ vs. Time for the Formation of Formaldehyde Dimethylhydrazone

FORMATION OF FDMH

Temperature: 30°C
Solvent Ether
UDMH = 0.20M, 250ml
Oxygen 91 ±0.5 mmole
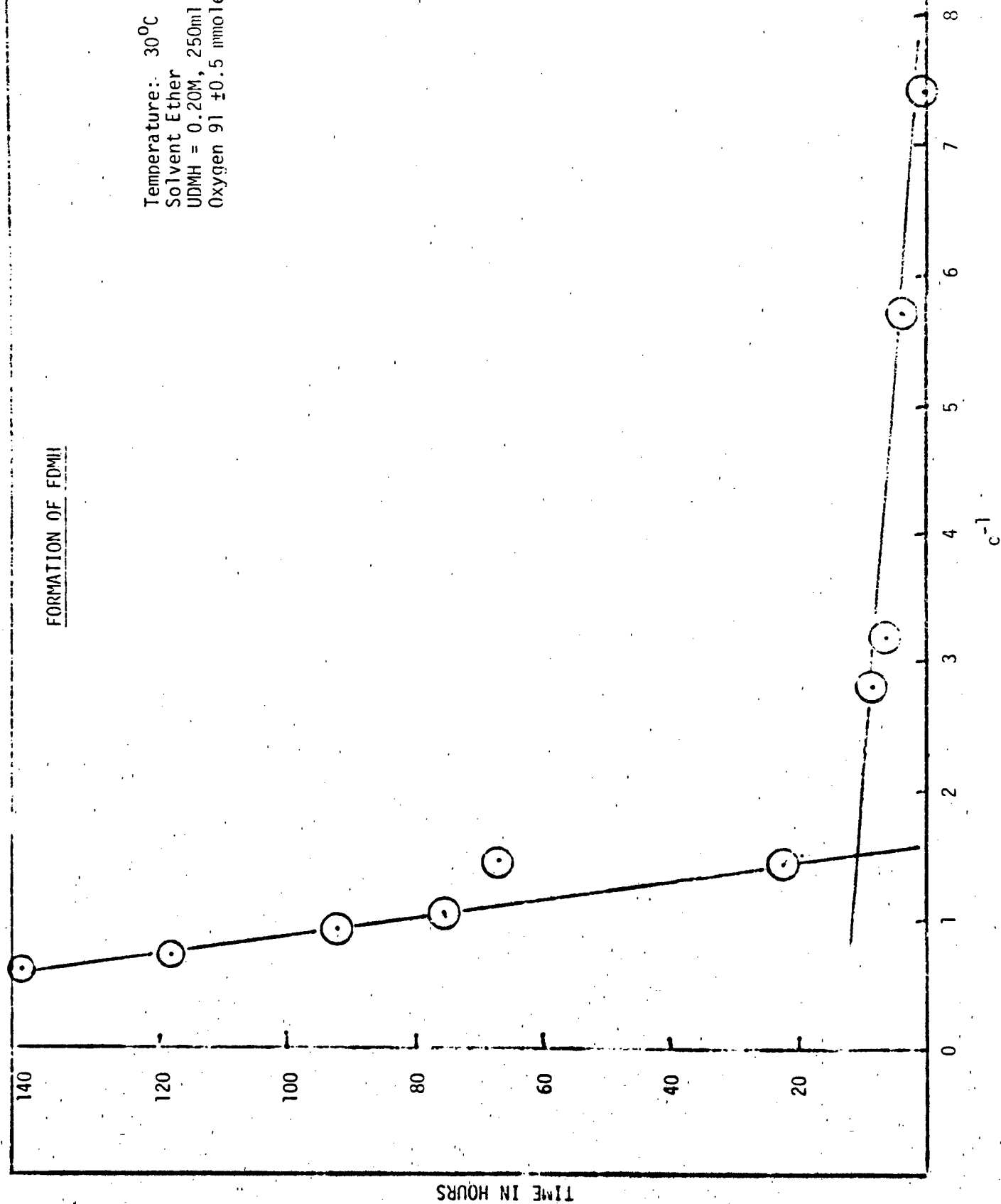
c^{-1}

TIME IN HOURS

Contribution from the Department of Chemistry

University of Florida, Gainesville, Florida 32611

SYNTHESIS OF MONOMETHYLHYDRAZINE IN NONAQUEOUS SOLVENTS

by

Sampat R. Jain, Milap A. Mathur, and Harry H. Sisler

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Introduction

Interest in the synthesis of hydrazine, monomethylhydrazine, and 1,1-dimethylhydrazine has developed because of interest in their use as rocket fuels. The synthetic processes for preparing substituted hydrazines disclosed in the literature are, in most instances, cumbersome, necessitating as they do the separation of substitute hydrazines from dilute aqueous solutions. The isolation of hydrazines from an aqueous solution requires multiple unit operations and, therefore, is expensive. Apart from the cost, some of the processes are known to involve intermediates that are toxic and hazardous. For example, in the well-known nitrosoamine process for the synthesis of 1,1-dimethylhydrazine, N-nitrosodimethylamine which is an intermediate in the process has been found to be carcinogenic[1]. This has resulted in the process being abandoned in the U.S.A. In the widely used modified Raschig process[2,3], the hydrazines are obtained in dilute

aqueous solution with the disadvantages associated therewith. In other processes such as in the urea process[4] and the hydroxylamine-O-sulfuric acid process[5], the hydrazines are obtained as aqueous solutions. Alternative procedures for synthesizing the substituted hydrazines are, therefore, needed.

One of the reactions[6-9] which has been seriously investigated as the basis for an alternative process in recent years is the chloramination reaction reported by Sisler et al[10-14]. The formation of hydrazine or alkyl substituted hydrazines by the reaction of gaseous chloramine with liquid ammonia or liquid amines was demonstrated earlier[11,12]. However, a large ratio of amine to chloramine (of the order of 400:1) has to be employed in order to obtain acceptable yields. Only scanty information is available in the open literature on the synthesis of monomethylhydrazine[2,8,11]. Most often this compound has been isolated as a derivative, rather than as the free hydrazine. The actual isolation of monomethylhydrazine has thus far not been discussed in the open literature.

From the recovery point of view, the synthesis of monomethylhydrazine in nonaqueous solvents is desirable. In aqueous solutions, it forms hydrogen bonds with water, making its isolation by distillation difficult. In this paper an attempt to synthesize monomethylhydrazine in nonaqueous solvents by the chloramination of methylamine is reported.

Experimental

Materials and Analyses. All solvents used were reagent grade. Monomethylhydrazine as obtained from Aldrich Chemicals was refluxed over KOH

pellets in an atmosphere of nitrogen. The fraction boiling at $87.5^{\circ}C$ was collected and used for the chloramination and other studies. Chloramine was produced by the gas phase reaction of ammonia and chlorine using a generator similar to that described by Sisler et al[10]. Chloramine was produced at the rate of about 0.1 mole per hour. Ammonia-free chloramine solutions in ether were prepared by passing the effluent gases from the chloramine generator through ether and removing the dissolved ammonia by passing the solution through a column of anhydrous copper sulfate. The concentration of chloramine in the ether solution was determined iodometrically. The hydrazines were determined by the iodate method[2]. The proton magnetic resonance spectra were recorded on a Varian Associates A-60-A spectrometer. The gas chromatographic data were obtained on a Varian model 3700 gas chromatograph equipped with a CDS111 data analyser and Soltic model 552 integrater recorder. A 6 ft Carbowax Column having the composition 10% Carbowax 20M + 5% KOH on Chrom WAW, 80/100 mesh was used. Unless otherwise stated, the chromatographs were obtained at the following settings; injector temperature, $170^{\circ}C$, Column temperature, $80^{\circ}C$, He flow rate 20 ml/min., thermal conductivity detecter temperature, $160^{\circ}C$, thermal conductivity current 150 mA and filament temperature $180^{\circ}C$. A Nester/Faust spinning band column was used for fractional distillation.

Symmetrical hexahydro-1,4-dimethyltetrazine was prepared[15] by reacting formaldehyde with monomethylhydrazine. Its melting point was found to be $124-5^{\circ}C$ (reported $122-4^{\circ}C$); analysis, found, C, 41.34, H, 10.41 and N, 48.23; calcd. for $(C_2H_6N_2)_2$; C, 41.36, H, 10.41 and N, 48.28. The mass spectrum contained a peak at m/e, 116. The nmr spectrum also matched well with that reported in the literature[15].

Reaction of the Chloramine-Ammonia Mixture with Methylamine in the Presence of KOH. In a typical experiment, potassium hydroxide pellets (0.53 mole) were dissolved in 150 ml. anhydrous methanol. A solution of methylamine in methanol was prepared by passing gaseous methylamine through it. The amine solution (175 ml. 1.22 mole of CH_3NH_2) was transferred to the KOH solution taken in a reaction vessel previously flushed with nitrogen. The exit of the reaction vessel was connected to a dry ice-acetone condenser. The inlet of the vessel was connected to the chloramine generator and the mixture treated with the NH_2Cl-NH_3 effluent of the chloramine generator at room temperature for 105 minutes, which corresponds to the introduction of 0.175 mole of chloramine. During the course of the reaction a white solid separated and the color of the solution gradually changed to faint yellow. After the chloramination, the reaction mixture was allowed to stand at room temperature to allow volatile gases to escape. The hydrazine content of the remaining mixture was estimated at this stage by titrating against standard (0.025 M) iodate solution. The formation of the N-N bonded material corresponded to 0.146 mole, i.e., 83.5% yield based on chloramine. When this mixture was allowed to stand overnight at room temperature, keeping the reaction vessel open to the atmosphere via a drying tube containing Drierite, the concentration of the N-N bonded material dropped to 0.108 mole.

The solution was decanted. The solid material was washed several times with ether and dried under vacuum. The total amount of solid material weighed 7.6 g. A portion of this material was crystallized by dissolving in water and precipitating with ethanol. The chloride analysis of the

material showed it to be pure KCl. (Found, Cl 47.64; calcd. 47.55%).

The methanol solution was fractionated on a spinning band column which had been earlier flushed with nitrogen. The liquid distilling below $65^{\circ}C$ was collected in two fractions. The one collected below $60^{\circ}C$ was found to contain the volatile amine and methanol. Although no monomethylhydrazine was picked up on the gas chromatograph, the iodate test showed that a hydrazine in trace amounts (0.0027 mole) was present. The second fraction ($60-65^{\circ}C$) was mostly methanol, but contained a hydrazine in small amounts (.0039 mole). No monomethylhydrazine peak was observed on the gas chromatograph.

When the volume of the liquid in the distillation flask was reduced to $\sim$ 30 ml., the mixture was transferred to a 100 ml. flask. After addition of fresh KOH pellets ($\sim$ 3 g.), it was subjected to fractional distillation on a mini glass apparatus having a Vigreux column and distilled under a nitrogen atmosphere. All the fractions collected between $83-113^{\circ}C$ showed the presence of monomethylhydrazine on the gas chromatograph. The major fraction distilling between $86-87.5^{\circ}C$ gave the following data (Table 1).

Table 1.

Retention Time (min.)	.51	.71	.85	1.85	3.32	4.70	10.05	11.20
% Area		.32	.43	.78	38.08	60.21	0.13	.03	.01

The retention times 1.85 and 3.32 min. corresponded to those of methanol and monomethylhydrazine, respectively. Thus, this fraction is free of water, but methanol appears to codistill with monomethylhydrazine. The various fractions when analyzed on the gas chromatograph gave the following results (Table 2):

Table 2.

Fraction	Distilling ranges °C	Amount (ml.)	Methanol (%)	MMH (%)	H_2O-Hydrazine (%)
1	83-86	1	61.3	34.3	None
2	86-87.5	4	38.0	60.2	None
3	87.5-106	1	35.0	61.0	None
4	106	3	11.0	9.0	77
5	106-113	4	None	None	95

The proton nmr spectrum of the second fraction showed only three peaks corresponding to δ values of 2.50, 3.08, and 3.98 ppm. with tetramethylsilane as external reference. The signals at higher field are the methyl proton resonances of monomethylhydrazine and methanol. The NH protons of monomethylhydrazine and OH protons of methanol appear as a single peak at δ 3.98 ppm.

The gas chromatograph of the 5th fraction showed a broad peak at a retention time 6.8 min. Both water and NH_2NH_2 when injected individually or as a mixture appeared in this time range. Similarly, the proton nmr spectrum of this fraction showed a single resonance peak at δ 4.67 ppm. with reference to tetramethylsilane as external standard. Therefore, it was not possible by these techniques to demonstrate conclusively the presence of NH_2NH_2. However, this fraction had strong reducing properties as shown by the iodate test. The amount of N-N bonded material present in this fraction was found to be 0.014 mole. The presence of NH_2NH_2 in this fraction was established by making the sulfate and benzaldehyde derivatives. To make the sulfate derivative, a 0.5 ml. portion of this fraction was chilled in ice, a few drops of conc. H_2SO_4 added to it resulting in the formation of

a white solid, which was washed with abs. ethanol and dried under vacuum.
The solid melted with decomposition at 258-260°C The reported melting point
of hydrazinium sulfate is 254°C[16]. The analysis of the solid by the iodate
method showed it to contain 21.53% N; expected for $N_2H_6SO_4$ is 21.65%. To
another 0.5 ml. portion of the fraction a few drops of benzaldehyde were
added resulting in a yellow solid, which, when dried under vacuum, melted
at 89-90°C; the melting point reported for benzalazine is 93°C. It was,
therefore, concluded that the fraction distilling between 106-113°C is a
mixture of NH_2NH_2 and water.

By the iodate test, the pot residue (mostly solid) after distillation,
was shown to contain hydrazine in small amounts. In order to estimate the
amount of NH_2NH_2 formed, the residue was dissolved in distilled water and
the NH_2NH_2 determined by the iodate method. The total NH_2NH_2 recovered
was estimated to be 14%, the remaining 86% of the N-N bonded material
being monomethylhydrazine.

Reaction of the Chloramine-Ammonia Mixture with Methlamine in the
Presence of Sodium Methoxide. A solution of anhydrous sodium methoxide
(18.0 g., 0.33 mole) in 140 ml. cold, anhydrous methanol was mixed with a
solution of 1.01 mole methylamine in 160 ml. methanol and the resulting
solution treated with the gaseous effluent of the chloramine generator for
two hours at room temperature. The outgoing gases were passed through an
overhead condenser kept at -75°C. Reaction occurred with the formation of
solid material and an intense yellowing of the solution. After standing at
room temperature for two hours, the mixture was found by the iodate pro-
cedure to contain 0.166 mole of N-N bonded compounds which corresponds to

82.3% yield of hydrazines based on chloramine used.

The solid material was separated under N_2 washed with ether and dried under vacuum (wt. 15.0 g.). Analysis show it to be NaCl.

Most of the liquid was distilled on a spinning band column. When the volu was reduced to ⌣ 50 ml., it was transferred to a small flask and fractionated under an N_2 atmosphere in an all glass distillation apparatus. Whereas no monomethylhydrazine was detected on the gas chromatograph from the fractions collected below 80°C, the fraction collected between 80-112°C contained monomethylhydrazine. The gas chromatograph of this fraction showed prominent peaks at retention times (% area), 1.8 (21.8), 3.3 (38), 4.7 (5.7), 6.4 (28.3) min. The peaks at retention times 1.8 and 3.3 min. can be assigned to methanol and monomethylhydrazine, respectively. The peak at retention time 4.7 min. can be assigned to formaldehyde methyl-hydrazone or its dimer, sym-hexahydro,1,4-dimethyltetrazine. Both these compounds when injected individually, the latter in benzene solution, gave a peak at retention time 4.75 min. The broad trailing peak with maxima at retention time 6.4 min. was suspected to be a multicomponent peak, pro-bably resulting from the presence of water and/or hydrazine and possibly from other side products. Beside these, there were at least four more peaks constituting about 6% of t'e mixture which may result from the presence of volatile components ⌐ince they appear at low retention times. Three of these peaks appear at retention time < 0.7 min. and were also present in lower boiling fractions. A small peak with an area 0.5% appeared at a retention time 1.6 min.

The proton nmr spectrum of the 80-112°C fraction gave only three prominent signals at δ 2.40, 3.21 and 4.38 ppm. with tetramethylsilane as external reference and could be accounted for as resulting from monomethylhydrazine, methanol and water, as in the case of the KOH reaction described above. The presence of NH_2NH_2 again could not be ascertained from the nmr spectrum. This spectrum was complicated at high amplitude by the presence of several additional signals. The formation of formaldehyde monomethylhydrazone could be inferred by the presence of a tiny quartet resulting from CH_2 protons in the range δ ,6.1-6.5 ppm. It is possible, however, that the dime of formaldehyde monomethylhydrazone, viz. sym. hexahydro,1,4-dimethyltetrazine is present, in which case the CH_2 proton resonance appears around δ 3.6 ppm.

The presence of NH_2NH_2 in the mixture was demonstrated by making its sulfate derivative. A few drops of conc. H_2SO_4 when added to a chilled 1 ml. sample of the mixture resulted in the formation of a white solid, which was washed with ethanol. On treating the solid with hot 80% ethanol, most of it dissolved leaving behind a small portion which was dried under vacuum. It contained N-N bands as well as SO_4^{--} and melted with decomposition at 258-60°C. The reported melting point of $N_2H_6SO_4$ is 254°C[16]. From the dissolved portion, a white crystalline material separated on cooling, which was washed with absolute ethanol and dried under vacuum. It melted sharply at 142°C which corresponds to the reported[2] melting point of $CH_3NHNH_2 \cdot H_2SO_4$ (142°C).

It is apparent, therefore, that NH_2NH_2 is formed in small amounts in this reaction, which is not surprising since ammonia from the chloramine generator was present in the reaction mixture.
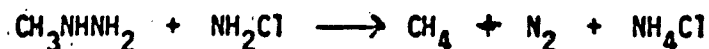
<u>Reaction of Chloramine with Methylamine in Nonaqueous Solvents in the</u>
<u>Absence of a Fixed Base</u>. In a typical reaction, methlamine (.375 mole) was
transferred under an oxygen-free nitrogen atmosphere to a flask containing
anhydrous ether at $-78^\circ C$, fitted with a condenser and a pressure-equalizing
funnel. Ammonia-free chloramine solution in ether (500 ml., 75 mmole
chloramine) was added rapidly from the funnel to the amine solution which
was stirred with a magnetic stirrer. No apparent reaction took place in
the initial stage. After complete addition of the chloramine solution, the
solution was brought to room temperature. A small amount of solid separated.
The solution was kept overnight. A test sample of the solution showed the
presence of NH_2Cl with only a very slight change (0.134 to 0.11 molar) in
concentration. It gave a negative test with IO_3^-. The mixture was then
refluxed for several hours. It still gave a negative test with IO_3^- indicat-
ing no formation of N-N bonded material. The solids formed had no oxidizing
or reducing properties and were found to be a mixture of CH_3NH_3Cl with a
trace of NH_4Cl.

The reaction was repeated in the presence of NH_3 by passing the effluent
gases of the chloramine generator into the amine solution; still there was
no indication of a reaction between chloramine and methylamine. The solid
material may have been formed by the decomposition of some of the NH_2Cl.

This experiment was carried out with and without ammonia using the
following solvent systems; xylene, methanol, diglyme, a mixture of diglyme
and ether, and a mixture of methanol and diglyme. In none of these cases
was any evidence for the formation of N-N bonded compounds found as shown
by the IO_3^- test.

Reaction of Chloramine with Monomethylhydrazine. This reaction was
carried out under different experimental conditions to determine (a) the
products of reaction and (b) the relative reactivity of chloramine toward
methylamine, monomethylhydrazine, and KOH. There is no report of the reac-
tion of chloramine with monomethylhydrazine in the literature.

(1) Reaction in the presence of ammonia. Monomethylhydrazine (0.1
mole) was dissolved in 75 ml. absolute methanol, cooled to $0^{\circ}C$, and treated
with the effluent gases from the chloramine generator for one hour, keeping
an overhead condenser at $-78^{\circ}C$ at the exit. Reaction occurred quickly as
shown by the change in color to light yellow. After about 20 min. of chlora-
mination, the color was discharged. At the end of the reaction, a colorless
solution was obtained with a white solid suspended in it. After allowing
the reaction to stand for two hours to allow ammonia escape, the solid material
was filtered, washed with ether, and dried. Neither the solution nor the
solid material, however, showed reducing properties by the iodate test.
The solid material was found to be ammonium chloride, more of which crystal-
lized out of methanol when the solution was distilled. The various frac-
tions of the distillate contained mixtures of ammonia and methanol as shown
by the gas chromatograph and the proton nmr spectrum. In the presence of
NH_3, the OH protons of methanol shift upfield. The pot residue contained
only methanol (99.97%) as shown by the gas chromatograph. It therefore appears
that monomethylhydrazine has reacted completely, giving NH_4Cl and gaseous
products. The overall reaction may be

$$CH_3NHNH_2 + NH_2Cl \longrightarrow CH_4 + N_2 + NH_4Cl$$

(2) <u>Reaction with ammonia-free chloramine</u>. The reaction of chloramine with monomethylhydrazine in the absence of ammonia was carried out using an excess of monomethylhydrazine. Monomethylhydrazine (25 ml.) was dissolved in 10 ml. anhydrous diethylether. The solution was cooled to $0^\circ C$ and reacted with 50 ml. of cold, ammonia-free, ethereal solution of chloramine (0.027 moles). An exothermic reaction ensued immediately and a white solid formed.

The mixture was stirred for 1 hour and the solids filtered. The ether solution was concentrated but showed no peak other than that of ether on the gas chromatograph in any significant amount. The solution had no reducing properties by the IO_3^- test. The solid material had reducing as well as mild oxidizing properties. After recrystallizing from acetone and drying under vacuum, it melted at $123\text{-}5^\circ C$. Analysis: Found C, 39.08; H, 9.06; N, 22.77; Cl, 28.97. Calcd. for $((CH_3)_2C=N-\overset{+}{N}H_2-CH_3)Cl$, C, 39.21; H, 8.98; N, 22.85; Cl, 28.98. The proton nmr spectrum showed three signals for CH_3-protons at δ 2.1, 2.22 and 2.80 ppm. and another broad signal at very low field, δ 9.82 ppm. The spectrum, apart from the low field signal, matched well with that of acetone-monomethylhydrazone[17]. The formation of this compound was confirmed by preparing this compound by treating methylhydrazine hydrochloride with acetone, and comparing its proton nmr spectrum with the product of the chloramination reaction.

It appears that the actual reaction product was methylhydrazine hydrochloride which was converted to acetone-methylhydrazone hydrochloride on recrystallizing from acetone. The formation of methylhydrazine hydrochloride could be a result of the reaction of monomethylhydrazine with NH_4Cl formed from the decomposition of chloramine.

(3) <u>Reaction of chloramine with a mixture of methylamine and monomethyl-</u>
<u>hydrazine</u>. This reaction was carried out in methanol to determine if chlora-
mine reacts preferentially with monomethylhydrazine in the presence of
methylamine. To a 0.6 molar solution of methylamine in 80 ml. methanol,
4.5 ml. (.08 mole) monomethylhydrazine was added and the solution treated
with the effluent from the chloramine generator for one hour. A clear solu-
tion which had no reducing property as shown by the iodate test was obtained
at the end of the reaction, thus showing that chloramine reacts preferen-
tially with monomethylhydrazine. As mentioned in an earlier experiment,
chloramine does not react with methylamine in the absence of a fixed base.

(4) <u>Reaction of ammonia-free chloramine with monomethylhydrazine in the</u>
<u>presence of KOH</u>. The objective of carrying out this reaction was to deter-
mine if chloramine reacts with monomethylhydrazine in the presence of a
fixed base such as KOH. KOH (.05 mole) pellets were dissolved in methanol
(25 ml.) and to this solution monomethylhydrazine (.05 mole) was added. This
mixture was treated with an ammonia-free solution of chloramine (.05 mole) in
250 ml. ether. This resulted in the formation of a white solid and the
solution developed an intense yellow color. The evolution of a gas was also
noticed. At the end of the reaction, the solid material was filtered and
the ether solution evaporated in a rotary evaporator. The color of the ether
collected was yellow but fades away on being exposed to the atmosphere. When
the volume of the mixture was reduced to $\sim$ 10 ml., it was examined on the
gas chromatograph. Whereas there was no peak corresponding to monomethyl-
hydrazine in the gas chromatograph, the solution possessed reducing properties.
Beside ether and methanol peaks, the other peaks observed were at retention

times (% area), 0.50 (2.3, 4.72 (1.1), 5.75 (.24), and 9.8-10.0 (2.2) min. The peak observed at 0.5 min. probably results from volatile substances. The peak at 4.72 can be attributed to sym.-hexahydro,1,1-dimethyltetrazine. A trace of H_2O is formed as shown by the peak at 5.75 min. The peak around 10 min. remains unidentified. The proton nmr supported these results; however, at high amplitude several other peaks appear.

It is clear that monomethylhydrazine reacts with chloramine even in the presence of KOH. The complexity of the reaction is evident from the appearance of color as well as nmr spectrum of the mixture.

Results and Discussion

It is apparent from these results that virtually no reaction takes place between chloramine and methylamine in the absence of a fixed base in the solvents tried. This is in contrast to the chloraminations of ammonia and dimethylamine which are known to occur in the absence of a fixed base in solvents to give hydrazine[13] and 1,1-dimethyltriazanium chloride[18], respectively. In the presence of a fixed base such as KOH or CH_3ONa, the chloramination of methylamine takes place readily resulting in the formation of monomethylhydrazine in significant amounts. In ether solution, Audrieth and Diamond[2] and Wiberg and Schmidt[19] also observed no reaction between chloramine and methylamine. This led Audrieth et al[2] to suggest that the presence of a fixed base is necessary to bring about the reaction.

It is interesting to note that whereas there is virtually no reaction between methylamine and chloramine in the absence of a fixed base, monomethylhydrazine reacts readily with chloramine in the absence of a fixed base.

As a matter of fact, the reaction between monomethylhydrazine and chloramine under these conditions is highly exothermic and complete. The preferential reaction of chloramine with monomethylhydrazine rather than methylamine in the absence of a fixed base was further demonstrated by the reaction of chloramine with a mixture of methylamine and monomethylhydrazine under these conditions. The result is unexpected in terms of the relative basicity of the two compounds since methylamine (pKa, 10.64) is more basic than monomethyl-hydrazine (pKa, 7.87) and might be expected to react preferentially with chloramine.

The hydrolysis of chloramine in alkaline solution is well-known[20]. However, in the presence of a fixed base, monomethylhydrazine reacts readily with chloramine. The fact that monomethylhydrazine can be recovered from the reaction between chloramine and methylamine in the presence of a fixed base suggests that chloramine reacts preferentially with the fixed base, resulting in the formation of an intermediate which then reacts with methylamine resulting in the formation of monomethylhydrazine. In such a situation, it would appear that monomethylhydrazine could remain unreacted as long as an excess of the fixed base and the amine are present.

Considering the various mechanisms proposed for the formation of hydrazines, it appears that a mechanism similar to that of Cahn and Powell[21] for the reaction of chloramine with ammonia in alkaline solutions

$$NH_3 + NH_2Cl \longrightarrow (N_2H_5Cl) \xrightarrow{OH^-} NH_2NH_2 + H_2O + Cl^-$$
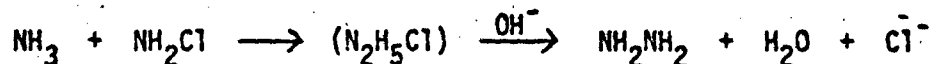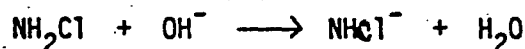
does not account for the reaction between methylamine and chloramine since chloramine reacts preferentially with the fixed base.

The preferential attack of chloramine on OH^- may be either the displacement of Cl^- by OH^- as proposed by Anbar and Yagil[20],

$$NH_2Cl + OH^- \longrightarrow NH_2OH + Cl^-$$

or abstraction of a proton by the OH^- ion forming a chloramide ion,

$$NH_2Cl + OH^- \longrightarrow NHCl^- + H_2O$$

which then decomposes to give imine radicals as proposed by Audrieth et al[22].

$$NHCl^- \longrightarrow (\overset{..}{N}H) + Cl^-$$

The imine radicals react with the amine to form a Lewis acid-base complex which then rearranges to give the hydrazine.

$$CH_3NH_2 + (\overset{..}{N}H) \longrightarrow [CH_3NH_2 \longrightarrow NH] \longrightarrow CH_3NHNH_2$$

The formation of hydroxylamine as a primary intermediate as proposed by Anbar and Yagil appears less likely since the synthesis of monomethylhydrazine by the reaction of methylamine with hydroxylamine has not been reported, nor was it realized in the present study when a caustic solution of hydroxylammonium sulfate was reacted with methylamine. Though the work of Drago and Sisler[23] has indicated that the mechanism proposed by Audrieth et al does not fit the evidence for NH_3-NH_2Cl reaction in aqueous OH^- solutions, it does appear to us to be the mechanism of choice for the methylamine-chloramine reaction in OH^- solutions.

The results indicate no unexpected products in the methylamine-chloramine reaction in the presence of KOH. However, in the presence of CH_3ONa, sym.-hexahydro-1,4-dimethyltetrazine and water were observed as additional products. These products are probably formed by the oxidation of monomethylhydrazine produced in the reaction by NH_2Cl or by atmospheric oxygen. This is indicated by the reaction of monomethylhydrazine with oxygen[24] or with chloramine. In both cases, the dimer of formaldehyde methylhydrazone and

water are obtained as reaction products. In the case of the methylamine—
chloramine reaction in the presence of CH_3ONa in methanol, the appearance
of water in the reaction products points to aerial oxidation of the mixture
during distillation or handling.

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THE FORMATION OF DIMETHYLMERCURY IN THE OXIDATION
OF MONOMETHYLHYDRAZINE BY MERCURIC OXIDE

Sir:

Considerations of laboratory safety as well as chemical interest
prompt us to prepare this brief communication concerning the chemistry
of monomethylhydrazine. We were seeking to prepare symmetrical dimethyl-2-
tetrazene by the oxidation of monomethylhydrazine by mercuric oxide.
E. Renouf[1] had reported in 1880 the preparation of symmetrical tetramethyl-2-
tetrazene by the reaction

$$2(CH_3)_2NNH_2 + 2HgO \longrightarrow (CH_3)_2N-N=N-N(CH_3)_2 + 2Hg + 2H_2O$$
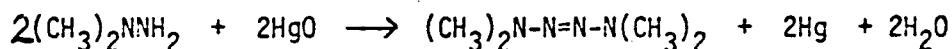
and it was hoped that monomethylhydrazine would react similarly. The
reaction was carried out in anhydrous ether and in addition to other pro-
ducts, a considerable amount of dimethylmercury was obtained. To our
knowledge, dimethylmercury has not previously been detected in the product
of mercuric oxide oxidations of methylhydrazines. A description of a
typical experiment follows.

Monomethylhydrazine (0.25 mole) in 160 ml. of anhydrous diethylether
was placed in a flask under a dry nitrogen atmosphere and 0.26 mole of yellow
mercuric oxide added over a 90 minute period with continuous stirring.
The exothermic reaction was controlled by constant cooling, keeping the
temperature below $5^{\circ}C$ during the addition of the mercuric oxide. The
reaction was stirred for a further 90 min. after which the liquid was
separated from the mercury and the remaining mercuric oxide by decantation.

The solution was analyzed in a Varian 3700 gas chromatograph using a Carbo-wax column. In addition to the solvent and air, three peaks were observed: two of these at retention times 5.81 and 4.83 min. can be attributed to water and to $CH_3NHN=CH_2$ or its dimer, respectively[2].
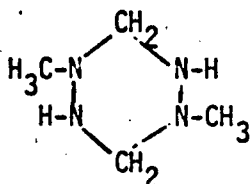
The third major component was isolated by drying the solution over $CaSO_4$ for 14 hours and evaporating it under reduced pressure. Approximately 1 ml. of a colorless liquid whose peak on the gas chromatograph had an identical retention time, viz. 2.42 min., with the third peak of the mixture. Based on the gas chromatographic analysis, this liquid contains about 97.9% dimethylmercury. The proton nmr of this material gave a single resonance at τ = 9.71 in CCl_4 with the tetramethylsilane as internal standard and in agreement with that reported for dimethylmercury[3]. Analysis: C, 11.41%; H, 2.92%; calcd. for $(CH_3)_2Hg$, C, 10.40%; H, 2.61%. The identification of this compound was further confirmed by comparing its infrared and mass spectra with those reported[4,5] for dimethylmercury.

The infra red spectrum of the product contained the following peaks: 2970-1900(s), 1640(w), 1400 (broad), 1240(w), 1110-1000(m), 750(s), 520(s) cm^{-1}. All these except the 1240 peak agree with the published data for dimethylmercury. The 1240 peak may result from an impurity.

The mass spectrum of this product is in excellent agreement with that expected for dimethylmercury. The precisely measured masses of the parent peaks agreed well with those calcd. for dimethylmercury as shown in Table 1.

Table 1.

Measured Masses	Calculated Masses for $(CH_3)_2Hg$
234.0209	234.0204
232.0162	232.0176
231.0158	231.0172
230.0139	230.0153
229.0133	229.0152

We are continuing to explore this and similar reactions. We recommend care in such processes to avoid the potential danger introduced by the possible formation of dimethylmercury.

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